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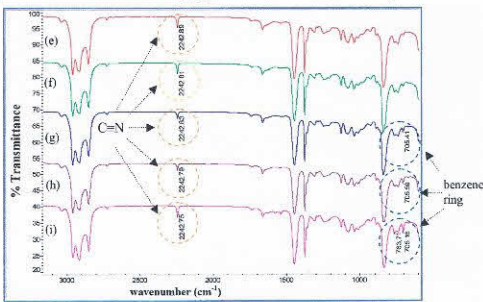
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#1266 Summary

| | |
|-----------------|---|
| Title | The Effect Of Styrene Monomer In The Graft Copolymerization of Acrylonitrile Onto Deproteinized Natural Rubber |
| Abstract | Graft copolymerization of acrylonitrile monomer onto the deproteinized natural rubber (DPNR) is an important process in modification of natural rubber (NR) to increase oil resistant. Coagulation at the beginning of the process was a problem causing the copolymerization did not occur. The process in either the presence or absence of styrene was investigated. The presence of styrene monomer could maintain the condition of emulsion therefore the coagulation could be prevented at the early reaction step. The influence of the concentration of styrene and ratio DPNR:monomer method on stabilization process was observed. The results showed that the addition of styrene could improve the stabilization process. The analysis of FTIR confirmed the functional group of C ^o N in the samples. The functional group of C ^o N at FTIR prove that is production of the polyacrylonitrile in the mixture. It has been reported that the effect of the concentration of styrene monomer to the emulsion stability is up to 1.5 wt% concentration of styrene at the ratio of DPNR to total monomer (M) of (70:30) wt%. The more total monomer concentration need the more styrene concentration to stabilize the graft copolymerization. The constant condition of the other ingredient were potassium persulfate (K ₂ S ₂ O ₈) 1 wt% as initiator, temperature of 65 °C and atmospheric pressure. |
| Keywords | acrylonitrile, emulsion stability, graft copolymerization, styrene |
| Authors | 1. Tuti Indah Sari 2. Asep Handaya Saputra 3. Setijo Bismo 4. Dadi R. Maspanger 5. Adi Cifriadi |
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THE EFFECT OF ACRYLONITRILE AND STYRENE COMPOSITION ON REDUCING THE PHYSICAL PROPERTIES DEGRADATION OF NATURAL RUBBER BY DIMETHYL ETHER

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ABSTRACT

Dimethyl ether (DME) is a clean fuel. However, the DME has moderate polarity, swells easily, and dissolves organic compounds. It can attack some sealing materials and other plastic components because of its low viscosity. Deproteinized natural rubber grafted acrylonitrile and styrene has potential use as a seal for DME storage. The copolymer DPNR-g-PAN/PS is expected to reduce the degradation of rubber due to DME. The resistance test parameters are swelling, shrinking, Fourier Transform Infrared Spectroscopy (FTIR) spectrum and the mechanical property changes after immersion. The results of this research indicate that the presence of acrylonitrile and styrene increased the mechanical properties DPNR. The increased concentration of acrylonitrile decreased the swelling of rubber; however, it also increased the shrinking of rubber. The increased concentration of styrene increased the swelling of rubber; however, it decreased the shrinking of rubber. The spectrum DPNR was more degraded than DPNR-g-PAN/PS after immersion. The surface morphology test also performed with a Scanning Electron Microscope (SEM). The morphology of DPNR-g-PAN/PS underwent a slight shrinking effect. However, DPNR underwent a huge shrinking effect.

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

1. INTRODUCTION

Dimethyl ether (DME), which is an alternative fuel has advantages, i.e.: a higher oxygen content, higher cetane number than diesel oil, and low boiling point and it is also non-toxic, non-teratogenic, nonmutagenic, and non-carcinogenic (Semelsberger, Borup, & Greene, 2006); (Arcoumanis, Bae, Crookes, & Kinoshita, 2008); (G. B. Li & L.-B. Zhou, 2008). Moreover, DME has superior atomization and vaporization characteristics, lower NO_x and SO_x than conventional diesel, and can be used in compression ignition (CI) engines without major modifications to the diesel configuration (Thomas, Feng, Veeraragavan, Cleary, & Drinnan, 2014); (Park & Lee, 2014).

However, DME has different chemical properties from LPG that has moderate polarity and high gas permeability to organic compounds such as plastics and rubber, it swells easily, and dissolves organic compounds (Nishimoto, 2011). It can attack some sealing materials and other plastic components because of its low viscosity (Arcoumanis et al., 2008).

The previous studies had resistance test using immersion method in DME. The swelling and mechanical properties of the rubber are parameters of the resistance test. Based on research by

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Li, et.al. the immersion of the rubber in a mixture of DME/diesel 20/80-wt% was reported to cause a corroded rubber seal (G. B. Li & L.-B. Zhou, 2008). In the progress of the research, Li, et al, found that rubber Nitrile Butadiene Rubber (NBR) was more resistant compared to other synthetic rubbers (Li, 2011).

On the other hand, natural rubber grafted acrylonitrile and styrene has potential use as a seal for DME storage. Natural rubber has excellent properties, good elasticity, high tensile strength, and best adhesion to metal. Polyacrylonitrile (PAN) is non solvent with hydrocarbons, chlorinated hydrocarbons ketones, diethyl ether, and acetonitrile (James E Mark, 2009). The presence of PAN in the mixture will also increase the insolubility and resistance to organic solvents (Nataraj, Yang, & Aminabhavi, 2012). Styrene is a good co-monomer in the stability of the graft-copolymerization process (Angnanon, Prasassarakich, & Hinchiranan, 2011; Prasassarakich, Sintoorahat, & Wongwisetsirikul, 2001); (T. I. Sari, Saputra, Bismo, Maspanger, & Cifriadi, 2015). According to studies conducted by Prasassarakich et.al., the oil and solvent resistance of NR can be improved by graft copolymerization with acrylonitrile (Prasassarakich et al., 2001). The tensile strength and oil resistant increased with the increasing percentage of grafting efficiency of acrylonitrile monomer (Prukkaewkanjana, Kawahara, & Sakdapipanich, 2014). Angnanon et.al. reported that the tensile properties and oil-swelling resistance of the blends increased with increasing acrylonitrile and styrene grafted (Angnanon et al., 2011).

The objective of research is to obtain copolymer DPNR-g-PAN/PS that has a high resistance to gas DME. The resistance is the potency to survive on the strength of the diffusion or corrosion caused DME that will decrease the mechanical and chemical properties of rubber. The copolymer DPNR-g-PAN/PS is expected to reduce the degradation of rubber due to DME based on simple research conducted by Sari et.al (T.I. Sari, Saputra, Maspanger, & Bismo, 2017). In this study, there are two steps processes. The first is the process of grafting copolymerization of acrylonitrile and styrene onto natural rubber. The characteristics of DPNR-g-PAN/PS by the chemical and mechanical properties test. The chemical properties tests are the spectrum copolymer by Fourier Transform Infrared Spectroscopy (FTIR) and cure characteristics by rheometer. The mechanical properties measurements are tensile strength, elongation at break, and hardness. The second is the resistant test of the rubber vulcanized with DME. The resistance test parameters are swelling, shrinking and the mechanical properties changes after immersion. The surface morphology test is also performed using Scanning Electron Microscope (SEM) analysis.

2. METHODS

2.1. Materials

The natural rubber latex with a high level of stabilized ammonia, containing about 59–60% of Dry Rubber Content (DRC) comes from South Sumatera, Indonesia. The acrylonitrile (AN \geq 99%) and styrene monomer (ST \geq 99%) were purchased from Sigma–Aldrich (SGP). 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 for vulcanized rubber. Dimethyl ether was purchased from PT. Bumi Tanggerang, Banten (INA). DPNR was prepared by mixing 0.1 wt% urea and 1 wt% SDS at room temperature for 60 minutes (Pukkate, Yamamoto, & Kawahara, 2008); (Suksawad, Yamamoto, & Kawahara, 2011). Then the latex was diluted to 20% by weight and followed by centrifugation at 6,000 rpm (T. I. Sari et al., 2015).

2.2. Graft-copolymerization AN/ST onto DPNR

The graft copolymerization of AN/ST onto the DPNR was carried out 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. $K_2S_2O_8$ was used as an initiator having 1 wt% of total monomer, and the reaction was allowed to proceed for 6 hours. The gross grafted DPNR consisted of the graft copolymer DPNR-g-PAN/PS, free DPNR, PAN, and PS-free homopolymer. The graft copolymer was synthesized using emulsion polymerization methods with a ratio of DPNR to Monomer(M) at (65:35); (70:30); (75:25) w/w, 95/5; 92/8; 90/10; 80/20 w/w for AN/ST. For 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. Grafting efficiency (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. Process of DPNR and Vulcanized DPNR-g-PAN/PS

The preparation of rubber copolymer from graft copolymerization to vulcanization process at a temperature of 150°C in press molding. The formulation of the DPNR and DPNR-g-PAN/PS vulcanized are tabulated in Table 1.

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

| Ingredients | Formulation (phr [*]) |
|-----------------------------|---------------------------------|
| DPNR-g-PAN/PS | 100 |
| Zinc Oxide (ZnO) | 5 |
| Stearic acid | 2 |
| 2-mercaptobenzothiazole/MBT | 1.8 |
| Sulfur | 2.4 |

^{*} phr = parts per hundred rubber by weight

2.4. Mechanical Property Test

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 by durometer and complied with ASTM D.2240-05 standard.

2.5. Swelling and Shrinking Test

The rubber vulcanized were immersed in DME liquid phase in 1.3 L pressure vessel. The mass change of these samples was investigated after the samples had been immersed in DME for several days and exposed to the atmosphere for 24 hours (Wu, Zhang, & Huang, 2008). The swelling is specified in percentage unit (%) as shown in equation (2) (G. Li & L. Zhou, 2008); (Hinchiranan, Wannako, Paosawatyanong, & Prasassarakich, 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 being soaked, and M_2 is the mass of the sample after being soaked. The samples after being soaked in DME are called wet samples and the samples after being exposed to the atmosphere for 24 hours are called dry samples.

2.6. Characterization

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 samples were prepared by pyrolysis and sokhlet-extraction method. The scanning electron microscope (SEM) model type ZEISS EVO 50 was used to analyse the surface morphology of DPNR and DPNR-g-PAN/PS before and after the immersion test in DME.

3. RESULTS AND DISCUSSION

3.1. Grafting Characteristics

Characteristics of grafting copolymer are indicative of the formation of DPNR-g-PAN/PS consisting of FTIR spectrum, Grafting Efficiency (GE), cure characteristics, and mechanical properties. Figure 1 shows a comparison of the FTIR spectrum of DPNR and grafting copolymers DPNR-g-PAN/PS. Comparison of the spectrum (a) and (b-d) in Figure 1 shown in their $\text{C}\equiv\text{N}$ group at wave number (b) 2242.26 cm^{-1} ; (c) 2242.22 cm^{-1} and (d) 2241.23 cm^{-1} , indicated PAN grafted on natural rubber chain. The presence of benzene groups at wave number (b) 704.12 cm^{-1} ; (c) 703.47 cm^{-1} and (d) 703.41 cm^{-1} indicated PS grafted on natural rubber.

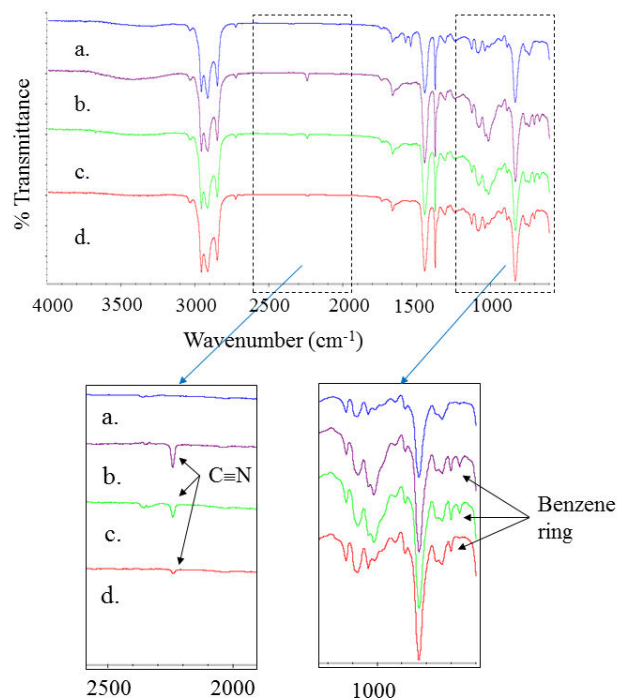


Figure 1 Spectrum FTIR DPNR and DPNR-g-PAN/PS at ratio DPNR/M 65/35
a. Spectrum DPNR; b. Spectrum DPNR-g-PAN/PS at ratio AN/ST 95/5; c. Spectrum DPNR-g-PAN/PS at ratio AN/ST 90/10; d. Spectrum DPNR-g-PAN/PS at ratio AN/ST 80/20

Figure 2a shows the effect of DPNR/M ratio on GE. The decreasing ratio of DPNR/M and ratio of AN/ST decreased the percentage of GE. This indicates immiscibility between AN and ST molecule. Possibly, the grafting copolymerization occurs only on the surface of latex particles. The increase addition of monomer AN and ST will not help in increasing GE; however, more free polymer are formed (Wongthong, Nakason, Pan, Rempel, & Kiatkamjornwong, 2013). This possibility also causes a decrease in GE in reaction time of more than 6 hours (Figure 2b).

Excess time causes the bond between polymer and DPNR unstable, and some have a broken back leading to a decrease in GE.

A decreased GE with increased reaction time is shown in Figure 2b. The experiments of DPNR/M in a ratio of 70:30 and AN/ST in a ratio of 92:8 occurred in reaction time of 6 – 10 hours. This reaction indicates that the decrease in GE began in reaction time for up to 7 hours. Figure 2b indicates that the optimum reaction time was 6 hours.

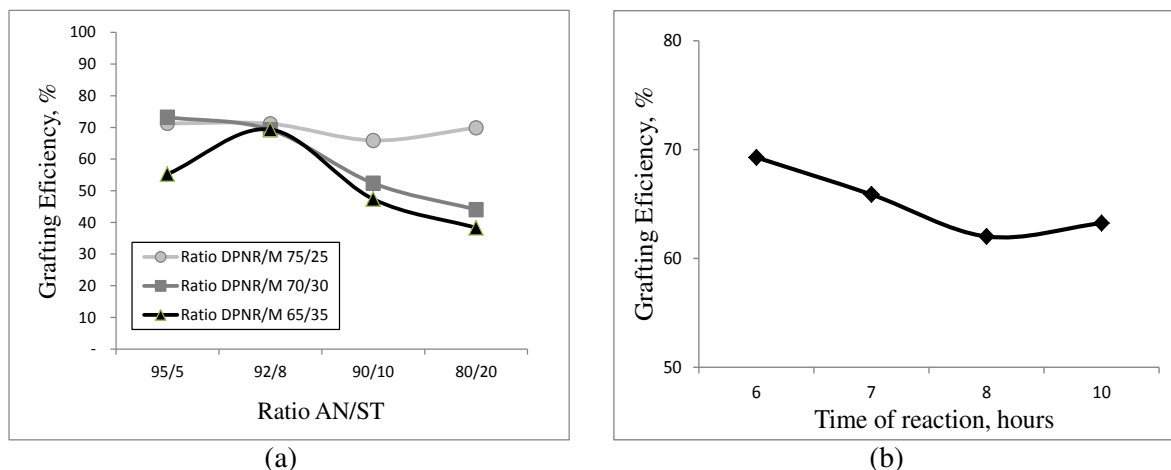


Figure 2 a. GE (%) with DPNR/M ratio and AN/ST ratio; **b.** GE (%) with time reaction (hours)

3.2. Characteristics of Cure

The effect of monomer concentration at an optimum cure is shown in Figure 3. From Figure 3, it can be seen that the optimum cure of vulcanized rubber grafting generally increased with the increasing total monomer. According to Man, optimum cure are increasing due to a decreased bond and allylic hydrogen in the mixture (Man, Hashim, & Akil, 2008). The presence of double bonds and allylic hydrogen plays an important role in the mechanism of cure of the vulcanized rubber (Ismail & Suzaimah, 2000); (Man et al., 2008). The decrease in double bond DPNR is caused by the entry of PAN and PS radicals breaking the double bond.

The optimum cure decreases in AN/ST ratio of 92:8 %-w. The decrease caused graft copolymer of this ratio at maximum conditions, accordingly the free polymer contained in the vulcanized rubber totaled less and reduces the mobility of macromolecule chains. The research conducted by Rahiman reported that the decrease in optimum cure and scorch time is caused by the increasing concentrations of acrylonitrile in NBR. This proves that the concentration of acrylonitrile affected the optimum cure and scorch time (Habeeb Rahiman, Unnikrishnan, Sujith, & Radhakrishnan, 2005).

Observations were also conducted on torque_{max-min} in Figure 3b. Torque_{max-min} is the difference between the maximum and the minimum torque. Figure 3b shows that torque_{max-min} rises significantly in AN/ST ratio of 92:8 %-w. Generally, for natural rubber vulcanized in unfilled form, the torque_{max-min} value represents the crosslink density (Tho, Kadir, & Hashim, 2002); (Habeeb Rahiman et al., 2005); (Man et al., 2008). Similarly, DPNR-g-PAN/PS copolymer is formed in AN/ST ratio of 92/8% w. Crosslink density increased due to the PAN and PS as a copolymer grafted and free polymer. This causes an increase in torque_{max-min}. However, the high crosslink density does not necessarily make the rubber hard and rigid, level -C-C- short length also determines the elasticity of rubber. The shorter the -C-C- increasingly elastic rubber (Bieliński & Stępkowska, 2013).

The decreasing optimum cure time and increasing torque_{max-min} in the ratio AN/ST 92/8 %-w, related to GE optimum and the possibly long-chains of grafting polymer PAN and PS. PAN and PS polymers with long-chain radical broke double bond natural rubber and are grafted in these positions. Although grafting efficiency is high, the double bond main chain of natural rubber is still higher. High grafting efficiency also led to an increased crosslink density; consequently, torque_{max-min} increased significantly.

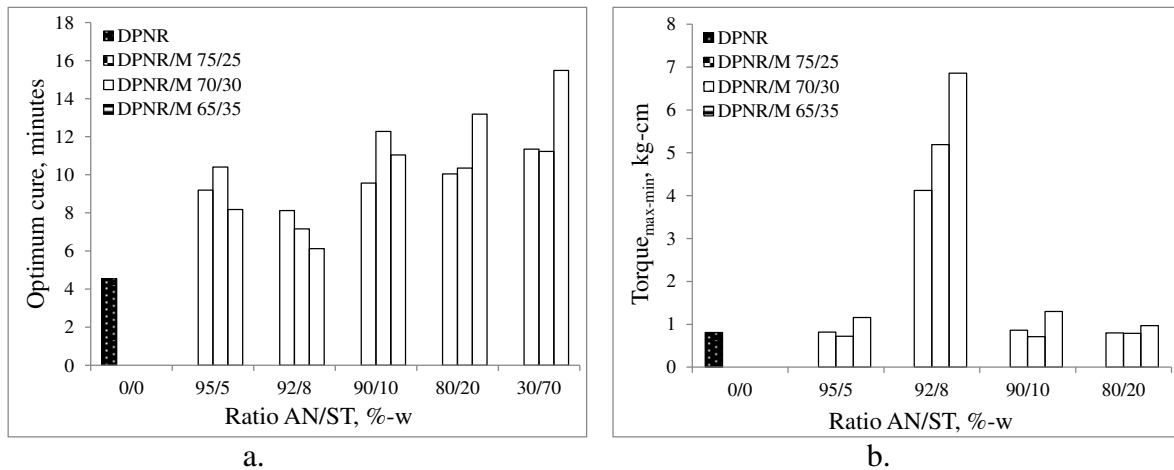


Figure 3 a. The influence of monomer concentration at DPNR optimum cure and DPNR-g-PAN/PS ;
b. The influence of monomer concentration at the torque_{max-min} DPNR and DPNR-g-PAN/PS

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

Characteristics of the mechanical properties of vulcanized copolymers are represented by tensile strength (TS), elongation at break (EB) and hardness. Figure 4a shows that the value of TS in DPNR-g-PAN/PS copolymers is higher than DPNR's. The increasing concentration of the total monomer increases the value of TS. PAN and PS as a free polymer in the mixture can also function as a filler which reinforces the mixture; thus, they can increase the value of TS. The value of TS is inversely proportional to the value of EB that decreases with PAN polymer and PS. However, the decreased value of EB is not particularly significant. The presence of PAN and PS as a free polymer makes vulcanized rubber slightly rigid because the polymers cover most of the pores of the rubber.

The mechanical properties of grafted vulcanized rubber are influenced by properties of polymer that grafted. The hardness of polymer will affect the flexibility of the rubber material, as well as types and molecular weight of polymers (James E. Mark, Erman, & Roland, 2013). Polyacrylonitrile (PAN) as a fiber polymer is hard and has a high molecular weight, whereas Polystyrene (PS) as a plastic polymer is softer than PAN. Polyacrylonitrile grafted onto natural rubber can increase TS and hardness (George, Maiti, & Varma, 2007); (Prukkaewkanjana et al., 2014). Figure 4a shows that the decreasing concentration of AN caused an increase in TS value. Figure 4b also shows the value of EB which decreases with the increasing concentration of ST.

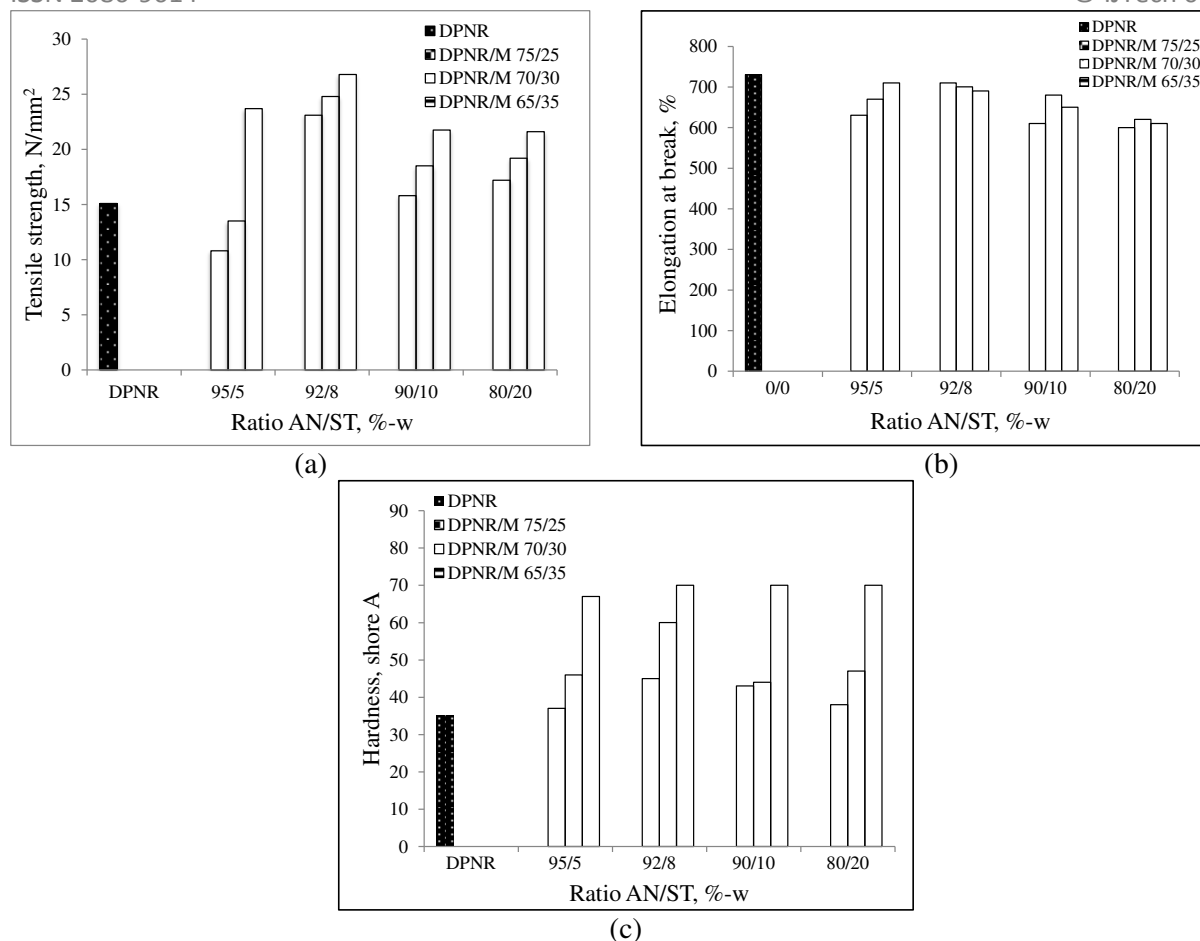


Figure 4 The influence of monomer concentration AN/ST to: a. tensile strength; b. elongation at break and c. hardness of vulcanized DPNR-g-PAN/PS

Several previous studies discussed the process of AN grafting onto natural rubber. The study by Angnanon et.al. reported that NR-g-AN/ST functioned as compatibility on blending natural rubber and NBR (Angnanon et al., 2011). In this study the presence of copolymer grafting increased the value of TS, but the variation in concentration of copolymer grafting did not significantly affect the value of vulcanized TS.

A research conducted by George stated that the increasing concentration of AN in the copolymerization process increases the value of TS and decreases the value of EB (George et al., 2007). Similarly, a research conducted 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 nitrile groups of the PAN. Therefore, a decrease in the content of PAN in rubber increases the rigidity of graft copolymer (Prukkaewkanjana et al., 2014). PAN and PS as grafted and as free polymers in vulcanized rubber improve hardness. Figure 4c shows that an increase in the concentration of total monomer increases hardness value.

3.4. Resistance Test on DPNR and DPNR-g-PAN/PS in DME

Measurements of resistance to DME are done by immersion of samples in a 1.3 L pressure vessel for several days. The observation of the vulcanized rubber is the mass change (swelling and shrinking), changes in mechanical properties (tensile strength, elongation at break and hardness), spectrum of rubber and surface morphology after immersion in DME.

3.4.1. Swelling and Shrinking After Immersion

The changing mass at wet measure which indicated swelling in DPNR and DPNR-g-PAN/PS is shown in Figure 5a. The results in Figure 5a show that the decreasing swelling of DPNR-g-PAN/PS occur in all concentration ratio of AN/ST when compared with DPNR. The increasing concentration of styrene increases swelling. The optimum point of AN/ST occurs in a ratio of 92:8, and DPNR/M in a ratio of 65:35 with the lowest swelling at 23.14%. This is caused by the level of crosslink density indicated by $\text{torque}_{\text{max-min}}$. Figure 3b, shows that at AN/ST ratio of 92/8 and DPNR/M ratio of 65/35 achieved the highest $\text{torque}_{\text{max-min}}$. According Tho, et.al, $\text{torque}_{\text{max-min}}$ value represents crosslink density (Tho et al., 2002). Figure 5a indicates that the swelling decreased with the increase in crosslink density.

Figure 5b is the mass change of dry measured after 24 hours. The decreasing mass changes at dry measured is called shrinking. Figure 5b shows that all DPNR and DPNR-g-PAN/PS samples have lost mass. However, the increased concentration of ST decreases mass loss. The lowest mass loss was -3.64% at AN/ST ratio of 80/20 and DPNR/M ratio of 65/35.

GE value in Figure 2a, Figure 5a shows that increasing GE decrease the swelling of DPNR-g-PAN/PS. However, unlike in Figure 5b, an increase in GE also increases shrinking in DPNR-g-PAN/PS.

Degradation experienced by DPNR-g-PAN/PS in AN/ST ratio of 80/20 in Figure 5b has the smallest value shrinking. This is probably caused by DPNR-g-PAN/PS in AN/ST ratio of 80/20 has polyacrylonitrile and polystyrene-free more than that in other AN/ST ratio. This phenomenon of free polymers acts as filler that fills crosslink rubber. As performed by Saputra, et al, in their study, such a phenomenon indicated 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 (Mikhailova, Baburina, Kalmykova, Deberdeev, & Kuttyrev, 2009). Likewise, Muniandy et al. (2012) also found that a filler loading resulted in a greater interaction between the rubber and the filler. The higher the extent of the interaction between the filler and the rubber matrix, the lower the swelling value (Muniandy, Ismail, & Othman, 2012)

The shrinking of mass in Figure 6 shows that the degradation DME to rubber vulcanized. The results in Figure 6a indicated that until 336 h there was a little difference between the percentage of shrinking of DPNR and DPNR-g-PAN/PS in AN/ST ratio of 92/8. However, in Figure 6b, there was a significant difference in the variation of DPNR/M ratio. There was a high difference from percentage of shrinking DPNR and DPNR-g-PAN/PS. Moreover, Figure 6b indicated that shrinking rate in DPNR/M ratio of 65/35 is smaller than in other lines.

Generally, Figure 6a and 6b indicated that shrinking rate declines, except for DPNR M ratio of 65/35. The rate of shrinking tends to form ramps and is linear in DPNR/M ratio of 65/35.

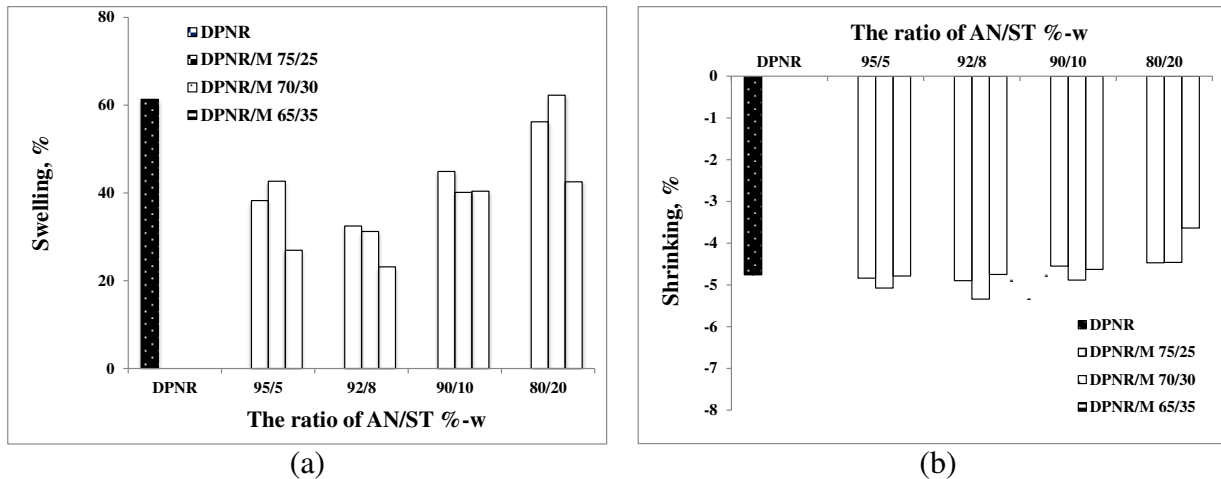


Figure 5 The swelling and shrinking of DPNR and DPNR-g-PAN/PS after immersion in DME 168 hours at (a). wet measured (b). dry measured

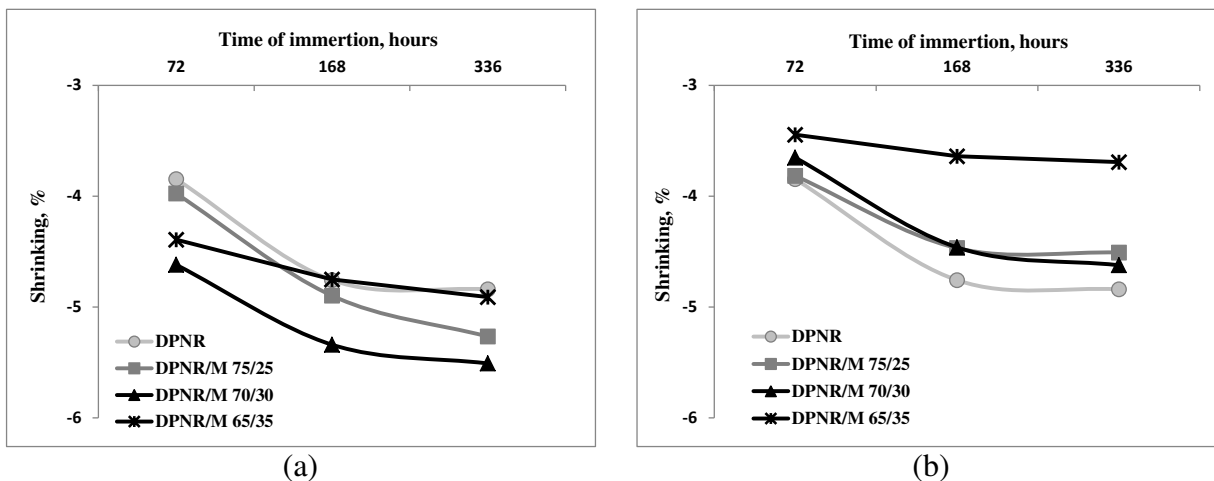


Figure 6 The mass degradation of DPNR-g-PAN/PS after immersed in DME (dry measure) a). at ratio AN/ST 92/8; b). at ratio AN/ST 80/20

3.4.2. Chemical and Physical Properties After Immersion

Figure 7 shows the spectrum of DPNR and DPNR-g-PAN/PS before and after immersion in DME. At the spectrum of DPNR after immersion, group C=C double bonds are lost at wavenumber 1576.59 cm^{-1} . Probably C=C double bonds broke and changed into C-C at wavenumber between $1000\text{-}700 \text{ cm}^{-1}$ and C-H at wavenumber 669.35 cm^{-1} and 3036.41 cm^{-1} . It was caused by interaction with the DME. In Figure 7c and 7d, the spectrum DPNR-g-PAN/PS before immersion is compared to the spectrum DPNR-g-PAN/PS after immersion. They have no broken C=C double bond; moreover, it is indicated that group C=C double bonds at wavenumber at 1538.74 cm^{-1} . There are only changed group C≡N at wavenumber 2242.57 cm^{-1} to 2242.27 cm^{-1} . And group of benzene from wavenumber 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 of these spectrums shows that DPNR is more degraded than DPNR-g-PAN/PS.

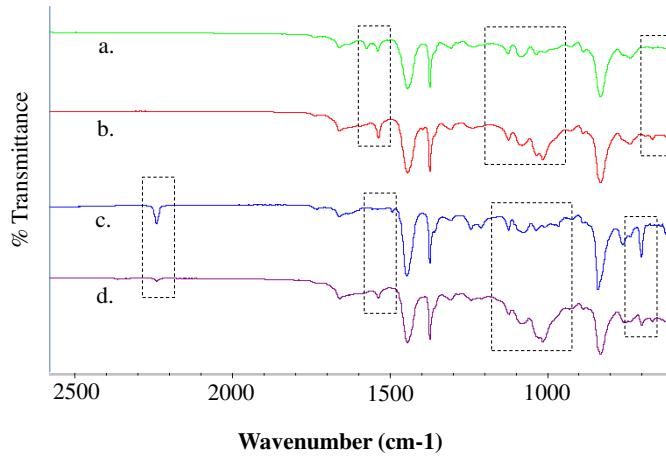


Figure 7 Spectrum FTIR of DPNR and DPNR-g-PAN/PS before and after immersion in DME (a). DPNR before immersion ; (b) DPNR after immersion; (c) DPNR-g-PAN/PS before immersion; (d) DPNR-g-PAN/PS after immersion

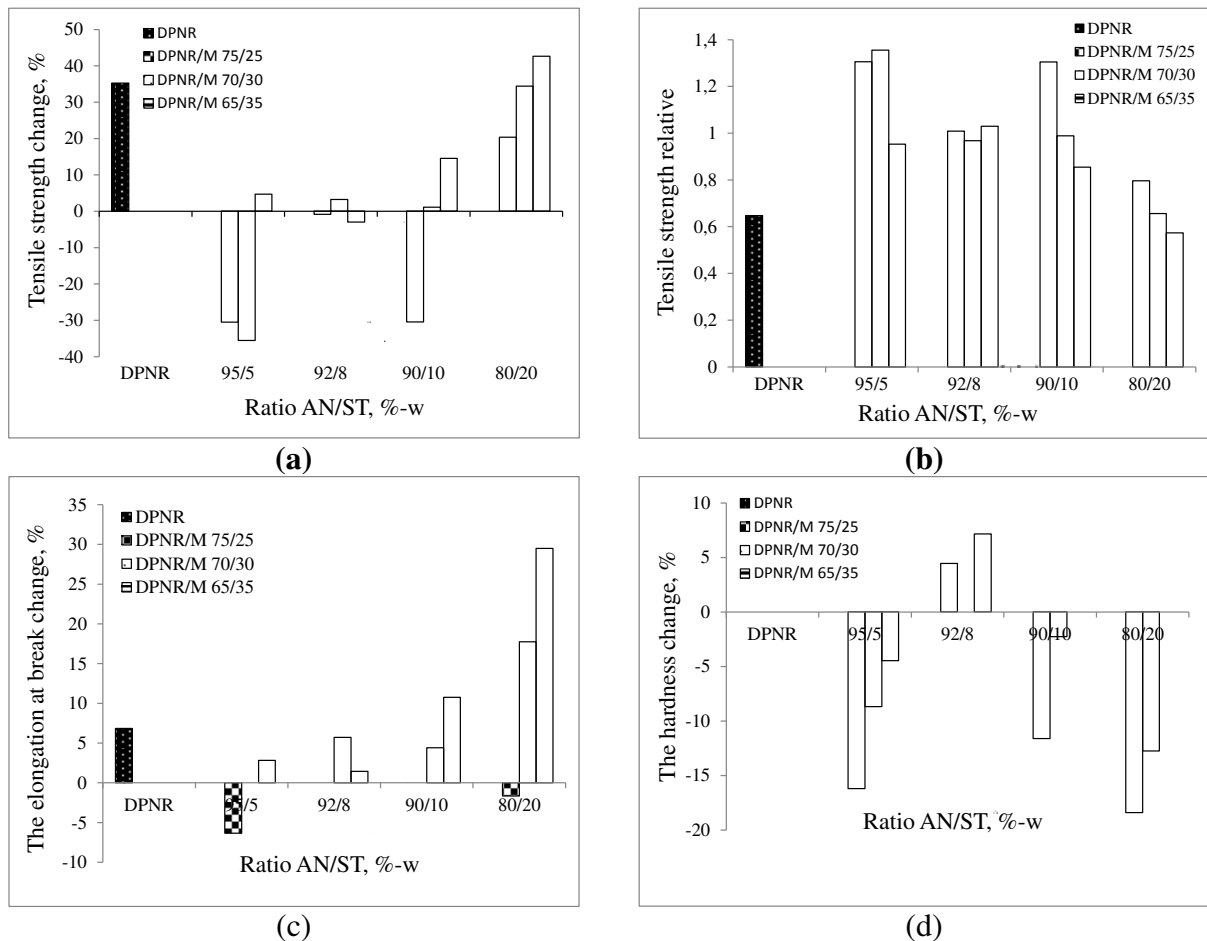


Figure 8 a. The tensile strength change; b. The tensile strength relative change; c. The elongation at break change; and d. The hardness change after immersed in DME

The Tensile Strength (TS) change is shown in Figure 8a. From the spectrum FTIR in Figure 8, the breaking of double bond C=C to C-C and C-H can also reduce strength and the elasticity of rubber. Therefore, TS and EB as shown in Figure 8a and 8c generally decrease.

Figure 8b shows that the tensile strength relative DPNR-g-PAN/PS is generally higher than DPNR. The exception is in AN/ST ratio of 80/20 where tensile strength tend to be lower than DPNR. It can be concluded that the relative result of high tensile strength of the dispersed DPNR phase surrounded by polyacrylonitrile phase as oil-resistant compound. As a result, swelling is restrained by polyacrylonitrile phase. However, in AN/ST ratio of 80/20, polyacrylonitrile activities are covered by polystyrene, which increases shrinking and then decreases tensile strength relative value. Figure 8d shows the hardness values increased after immersion. 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 hardness to increase.

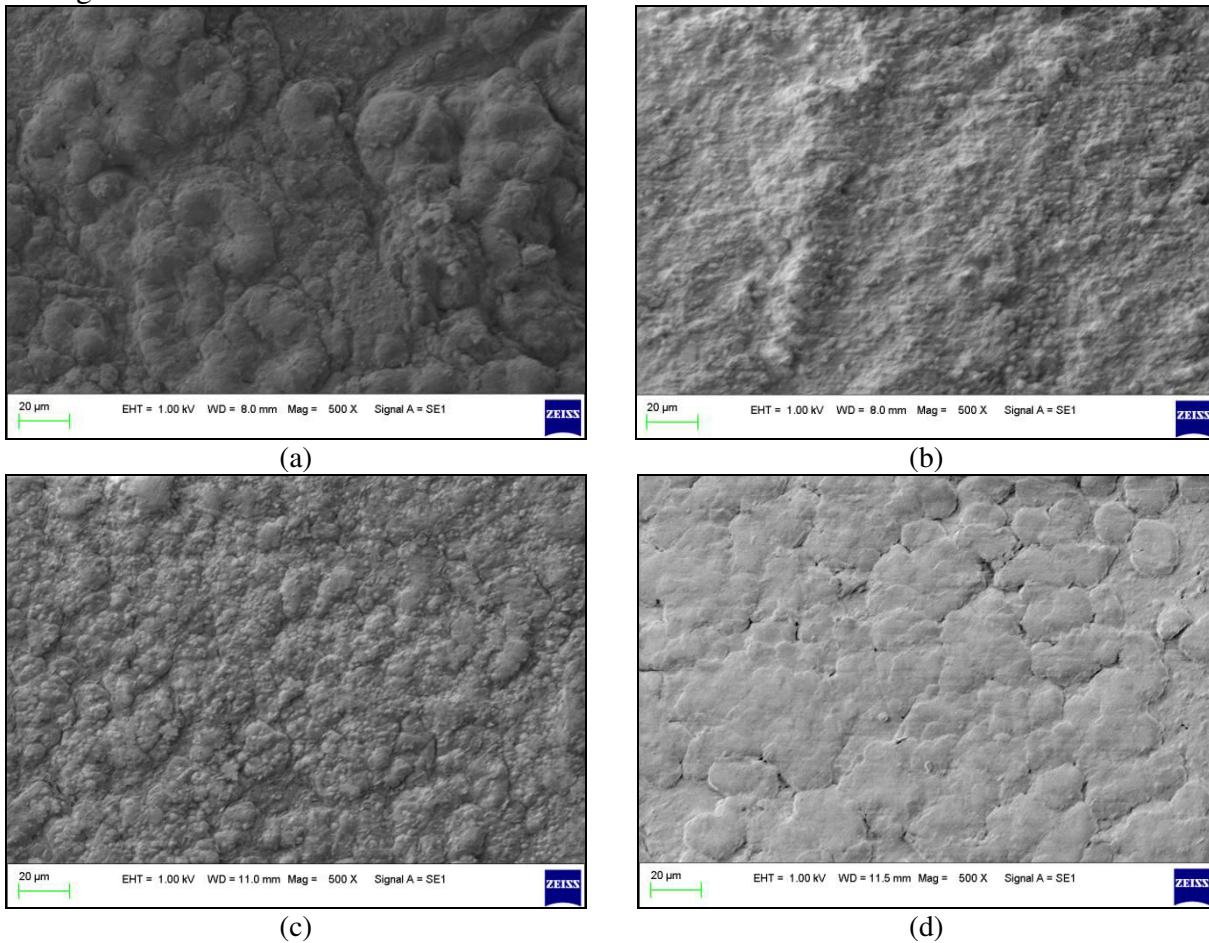


Figure 9 The surface morphology DPNR and DPNR-g-PAN/PS by SEM analysis before and after immersed in DME: (a) DPNR vulcanized before immersion; (b) DPNR vulcanized after immersion; (c) DPNR-g-PAN/PS vulcanized before immersion; (d) DPNR-g-PAN/PS after immersion

Analysis of surface morphology using ZEISS EVO 50 scanning electron microscope (SEM) was conducted at 500 times magnification to characterize the degradation behaviour of DPNR and DPNR-g-PAN/PS specimens before and after immersion in DME. Figure 9a and 9b show a difference between the morphology of DPNR before and after immersion in DME. Figure 9b shows that erosion of the material is because the absorption and desorption of DME into the rubber network. Possibly, there was a reaction between DME and some ingredients during DME absorption in the rubber. Erosion of material is called shrinking. The same thing happens in Figure 9c and 9d. In the Figure 9d shrinking occurs that causes morphological changes compared to Figure 9c. The surface in Figure 9d is smooth, flat and sallow in color. In the

Figure 9, it can be concluded that the morphology of DPNR-g-PAN/PS underwent a slight shrinking effect. However, DPNR underwent a huge shrinking effect.

4. CONCLUSION

This experiment is on production and resistance test of copolymer DPNR-g-PAN/PS in DME with the influence of acrylonitrile and styrene monomer. The results of this research can be concluded as follows: (i) the presence of acrylonitrile and styrene increased the mechanical properties of DPNR and DPNR-g-PAN/PS (ii) the increasing concentration of acrylonitrile decreased the swelling of rubber, yet it also increased the shrinking of rubber. The increasing concentration of styrene increased swelling of rubber; however, it also decreased the shrinking of rubber (iii) FTIR spectrum of DPNR was more degraded than spectrum DPNR-g-PAN/PS; (iv) the morphology of DPNR-g-PAN/PS underwent a slight shrinking effect. However, DPNR underwent a huge shrinking effect.

5. ACKNOWLEDGEMENT

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| | | Komentar |
|---|---|--|
| 1 | Format | Lihat betul format ang diminta QIR (Jenis huruf dan ukurannya, jumlah kata, corresponding author, dll,) |
| 2 | Styreneas a Stabilizer of Emulsion in theGraft Copolymerization Process ofAcrylonitrileonto Natural Rubber | <ul style="list-style-type: none"> - Judul ini menekankan pada styrene sebagai stabilizer, ok saja, tapi mungkin saja sudah banyak orang yang tahu bahwa styrene memang komponen yang membuat stabil. - Bagaimana kalau “stabilization process of Emulsion ...dst”, sehingga styrene nanti ditemukan sebagai komponen yang mampu menstabilkan |
| 3 | Graft copolymerization ofacrylonitrilemonomer onto deproteinated natural rubber (DPNR) withpotassium persulfate($K_2S_2O_8$) as initiatorat a temperature of 65^0C and atmospheric pressure is very difficult. | - Jangan “very difficult” yang menjadi penekanan, sebaiknya “very important process” |
| 4 | Coagulation at thebeginning of the processcauses the copolymerization was not occurred. Monomer styrene was used to improve emulsion stability untill the process occurred during the graft copolymerization time | <ul style="list-style-type: none"> - Sebaiknya ditonjolkan bahwa, Coagulation is the problem in copolymerization process - Sehingga perlu dilakukan penelitian tentang ini |
| 5 | The influence of concentration of styrene, ratio DPNR/monomerand loading initiator method on stabilization process was investigated. The results showed that introduction of adding styrene could improve stabilization process and analysis offourier transforminfrared spectroscopy (FTIR) confirmed the formation of the polyacrylonitrile-grafted-deproteinated natural rubber (PAN-g-DPNR) copolymers at wavelenghts 2242 to 2243 cm^{-1} . | <ul style="list-style-type: none"> - OK saja - Tonjolkan metoda dan cara penentuan keberhasilan |
| 6 | The results showedthatthe effect ofthe concentration ofstyrene monomerto theemulsion stabilityis up to1.5% w/wconcentration ofstyrene. It has been reported that increase ratio DPNR/monomer can increase stability emulsion ofthe graft copolymerizationprocess. RatioDPNR/monomerthat is starting to showa goodemulsion stabilitywas achieved in70/30w/w. While themethod of loading initiator $K_2S_2O_8$ continuouslydrop to drop (rate of ± 0.7 ml/min) made emulsionmorestablethan batch method. | <ul style="list-style-type: none"> - Penyampaian hasil → OK, tapi perlu perbaikan kalimat. - “The results showedthatthe effect ofthe concentration ofstyrene monomerto theemulsion stabilityis up to1.5% w/wconcentration ofstyrene.” Sebaiknya disampaikan saja bahwa diatas 1.5% w/w menunjukkan kestabilan, untuk komposisi DPNR/monomer berapa. Itu saja sudah cukup. - “While themethod of loading initiator $K_2S_2O_8$continuouslydrop to drop (rate of ± 0.7 ml/min) made emulsionmorestablethan batch method.” → kalimat ini tidak perlu |



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| 1 | RESULTS | |
| | 1. RESULT AND DISCUSSION should be RESULTS AND DISCUSSION | finished |
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| 2 | 4.Rise in temperature in the system can lead to collisions between particles sol with water molecules multiply thereby releasing electrolyte which is adsorbed on the surface of the colloid.... Please modify and revise this sentence | The temperature rise in the system can induce to collisions between sol particles and water molecules, therefore releasing electrolyte which is absorbed on the colloidal surface |
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THE EFFECT OF STYRENE MONOMER IN THE GRAFT COPOLYMERIZATION OF ACRYLONITRILE ONTO DEPROTEINIZED NATURAL RUBBER

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ABSTRACT

Graft copolymerization of an acrylonitrile monomer onto Deproteinized Natural Rubber (DPNR) is an important process in the modification of Natural Rubber (NR) to increase its oil resistance. However, coagulation at the beginning of the process was a problem causing a copolymerization foil to occur. The presence of a styrene monomer is therefore expected to improve the emulsion condition so that coagulation can be prevented in the early reaction step. For comparison purposes, the processes with and without styrene were investigated. The influence of the concentration of styrene as well as the ratio of the DPNR:monomer on the stabilization process were also observed. The results showed that the addition of styrene could improve the stabilization process as proven by Fourier Transform Infrared Spectroscopy (FTIR). The presence of the functional group of C≡N at FTIR proved the production of the polyacrylonitrile in the mixture. The investigation showed that the concentration of styrene monomer, which led to the emulsion stability, is up to 1.5 wt% concentration of styrene at the ratio of DPNR:monomer (M) of 70:30 wt%.

Keywords: acrylonitrile, emulsion stability, graft copolymerization, styrene

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1. INTRODUCTION

Natural rubber (NR) is a natural elastomer and a green commodity with properties such as high elasticity, strength, and power adhesion with metal, (Simpson, 2002). However, NR is not resistant to oil or organic solvent when it is compared to synthetic rubber. The chemical modification of NR with graft copolymerization is one of the means to improve certain properties, such as its oil or organic solvent resistance. 'Grafting' is a method for the modification of polymers, wherein monomers are bunched covalently onto the polymer chain, (Bhattacharya & Misra, 2004). Graft copolymerization initiated by chemical treatment is one of the most widely used methods for modifying natural rubber into a desired rubber product with good mechanical properties or chemical properties. In addition, NR is unsaturated rubber, therefore makes it easy to react with the monomer.

Only some monomers can interact with natural rubber. Two of them are Acrylonitrile (AN) and Styrene (ST). An acrylonitrile monomer has a high polarity, if it is compared with other monomers. According to Nagaty et. al., observed differences in grafting acrylonitrile, ethyl acrylate and methyl methacrylate on insoluble starch. The case concluded that the reactivity order was $AN > \text{ethyl acrylate (EA)} \approx \text{methyl methacrylate (MMA)}$, (Nagaty, Abd-Et.-Mouti, & Mansour, 1980).

Acrylonitrile is also a functional group in the Nitrile Butadiene Rubber (NBR). The higher the content of AN in the NBR, will be the higher the oil resistance, fuel resistance, tensile strength, hardness, abrasion resistance, gas impermeability, heat resistance, and plasticizer compatibility, (Simpson, 2002). Acrylonitrile grafting on natural rubber is expected to have properties close to NBR rubber. In other research, AN, as a monomer grafted onto the natural rubber, was observed (Yamamoto, Sawada, & Kawahara, 2007). The presence of Polyacrylonitrile (PAN), as a homopolymer in the mixture will also increase the insolubility and resistance to organic solvents, (Nataraj, Yang, & Aminabhavi, 2012).

Unfortunately, there are difficulties in reacting monomers or polymers onto NR, because of the unstable mixture in NR latex phase at the point of temperature reaction. The unstable mixture results in coagulation of the NR at the earliest time during the reaction. Coagulation at the beginning of the process causes trouble and stops the copolymerization. The presence of the styrene monomer in the reaction makes the process stable and it impacts the specified reaction time.

In previous works, the addition of ST is to assist the process of grafting Maleic Anhydride (MA) onto NR, (Saelao & Phinyocheep, 2005); (Wongthong, Nakason, Pan, Rempel, & Kiatkamjornwong, 2014). In other works, the addition of ST onto isotactic polybutene-1 occurs, (Zhao, Ma, Yao, & Huang, 2011). During the reaction, ST can behave as an electron donor to activate the carbon-carbon double bond of the MA molecule by composing a Charge Transfer Complex (CTC) between them, which highly activates the weakly reactive double bond of MA towards the macroradicals of the natural rubber, (Wongthong et al., 2014). It was found that the presence of the styrene monomer with MA or isotactic polybutene-1 in the grafting reaction can increase both grafting efficiency and grafting yield, (Wongthong et al., 2014; Zhao et al., 2011).

In the previous researches, ST had been used as a co-monomer for the grafting of acrylonitrile onto an Ethylene-Propylene-Diene Monomer (EPDM), (Qu, Shang, Liu, & Zhang, 2002); as well as for natural rubber (Angnanon, Prasassarakich, & Hinchiranan,

2011; Prasassarakich, Sintoorahat, & Wongwisetsirikul, 2001); and for Chlorinated Polyethylene (CPE), (P. Luo & Wu, 2012). Additionally, the use of ST as a co-monomer can promote higher grafting efficiency (Angnanon et al., 2011).

In this research, the graft copolymerization of AN and ST onto natural rubber is conducted by free-radical emulsion polymerization. The natural rubber latex is concentrated with a low protein content. This study was performed under operating conditions at a temperature (T) = 65 °C and a pressure (P) = 1 atm with potassium persulfate $K_2S_2O_8$ as the initiator. This study also observes the effect of adding ST to the process of grafting AN onto natural rubber, the comparison between the presence and absence of styrene, the variation of AN/ST concentration ranging from 0 – 5 wt% and the variation of the ratio of deproteinized natural rubber (DPNR) to the total monomer (M), resulting in (60:40) and (70:30) wt%, respectively in the grafting process.

2. EXPERIMENT

2.1. Materials

The natural rubber latex with a high level of stabilized ammonia, containing about 59 – 60 % of Dry Rubber Content (DRC) from South Sumatera, Indonesia. Sodium Dodecyl Sulfate (SDS ~90%) and potassium persulfate (*peroksodisulfat*) ($K_2S_2O_8 \geq 99\%$) were purchased from Merck (Germany). The acrylonitrile (AN $\geq 99\%$) and styrene monomer (ST $\geq 99\%$) were purchased from Sigma–Aldrich (SGP). Acetone was purchased from PT. Bratachem (INA) and nitrogen gas was purchased from PT. Trijaya Gasesindo (INA). DPNR was prepared by an incubation of NR latex with 0.1 wt% urea and 1 wt% SDS at room temperature for 60 minutes, (Pukkate, Yamamoto, & Kawahara, 2008; Suksawad, Yamamoto, & Kawahara, 2011; Wongthong, Nakason, Pan, Rempel, & Kiatkamjornwong, 2013; Yamamoto, Nghia, Klinklai, Saito, & Kawahara, 2008). Then the latex was diluted to 20% by weight and followed by centrifugation at 6,000 rpm. The measurement of the total nitrogen content of the rubber was achieved by the Kjeldahl method, (Wongthong et al., 2013). The high protein in the NR can act as an inhibitor in the polymerization reaction, (Tho, Kadir, & Hashim, 2002). It was found that the protein content of the latex significantly decreased from 1.88 wt% to 0.88 wt%.

2.2. Graft-copolymerization Process

The graft-copolymerization of the AN monomer onto the DPNR (DPNR-g-PAN) was carried out according to the following steps. The DPNR latex, SDS (0.67 w/w % of rubber) and distilled water were first charged into a 400 ml glass reactor equipped with hot plate, magnetic stirrer and nitrogen gas inlet. The mixture was stirred at about 300 rpm, under a nitrogen atmosphere for 30 min to remove the dissolved oxygen in the latex. The mixture of the AN and ST monomers was fed dropwise into the reaction vessel. $K_2S_2O_8$ was used as an initiator, having 1 wt% of total monomer and its solution was slowly added dropwise. The reaction was allowed to proceed for 6 hours and the mixture was treated with acetone and distilled water. The coagulum was dried at room temperature and later on, it was to be made into rubber sheet. In this research, the graft copolymer was synthesized from the graft copolymerization of AN onto the DPNR with the presence of a little concentration of the styrene monomer, using an emulsion polymerization technique at a range from 0 – 5 % by weight of styrene monomer

concentrations. The ratio of DPNR to M in this research were (60:40) and (70:30) wt%, respectively.

2.3. Characterization

Fourier transform infrared spectroscopy (FTIR) spectra of the rubber and graft copolymers were recorded using a Nicolet iS5 spectrometer (Thermo Scientific) in the range of 500–4000 cm^{-1} .

3. RESULTS AND DISCUSSION

3.1. The Effect of the Addition of Styrene as a Co-Monomer

The thermal initiator system used in this work was conditioned by using $\text{K}_2\text{S}_2\text{O}_8$ 1 wt% as an initiator at a temperature of 65 °C. To study the effect of the addition of ST varied from 0 – 5 wt% of total monomer, while the total monomer and other ingredients were kept constant. The effect of the styrene monomer concentration on the stability of the graft process acrylonitrile is shown in the Table 1. The term 'stability of process' means the process is stable without any coagulation at the beginning of the reaction. Furthermore, polymerization reactions could take place until the reaction time is reached. Table 1 shows that stable process conditions at the time of styrene concentrations started from 1.5% by weight in relation to the total monomers. Concentrations below 1.5% by weight of the total monomer cause latex coagulation, so the reaction was interrupted due to a significant change in viscosity, as a result of the coagulation.

Table 1. The condition of process by adding ST at concentrations from 0 – 5wt% and the ratio of DPNR to M = (70 : 30) wt%

| No. Spectra | Concentration | | Condition of process |
|-------------|---------------|------|--------------------------|
| | AN % | ST % | |
| b | 100 | 0 | Coagulation before 1 h |
| c | 99.5 | 0.5 | Coagulation after 1 h |
| d | 99 | 1 | Coagulation after 2 h |
| e | 98.5 | 1.5 | No coagulation until 6 h |
| f | 98 | 2 | No coagulation until 6 h |
| g | 97.5 | 2.5 | No coagulation until 6 h |
| h | 97 | 3 | No coagulation until 6 h |
| i | 95 | 5 | No coagulation until 6 h |

The characteristics of the product were investigated under FTIR analysis. FTIR test results in Fig. 1 show the nitrile group at Spectrum (e) at wave number 2,242.89 cm^{-1} , whereas Spectra (b) until (d), did not indicate the presence of the functional group of $\text{C}\equiv\text{N}$. These Spectra (b) until (d) are similar to Spectrum (a), which is the spectrum of pure natural rubber. According to Smith, the nitrile group ($\text{C}\equiv\text{N}$) could be seen at wave numbers 2,240 – 2,260 cm^{-1} , (Smith, 1979), and according to the Nacimiento et al., polyacrylonitrile is indicated at wave number 2,242 cm^{-1} , (Nacimiento, Alcántara, González, & Tirado, 2012). In previous work, a peak of $\text{C}\equiv\text{N}$ could be found at 2,244 cm^{-1} , (Moafi, Fallah Shojaie, & Ali Zanjanchi, 2011).

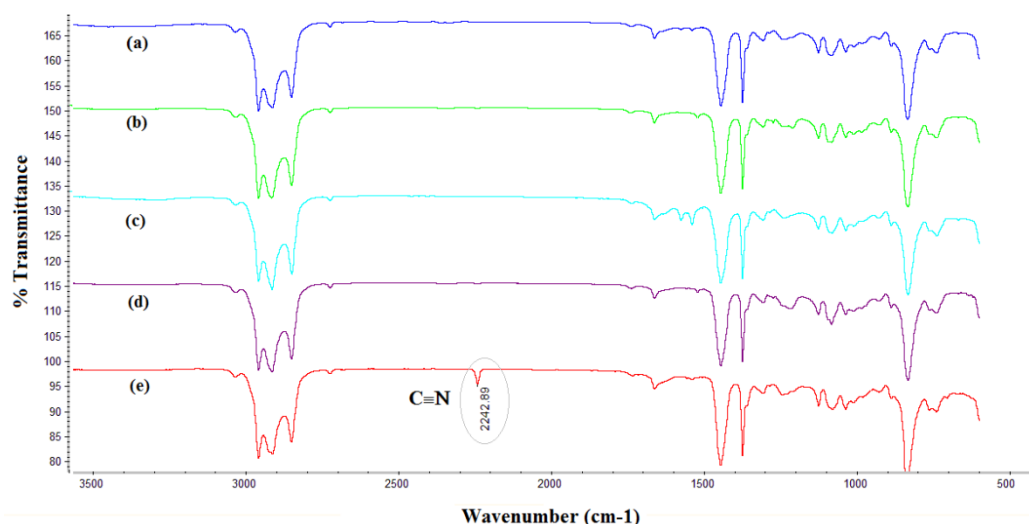


Fig. 1. FTIR spectra of copolymer with the addition of styrene ranging from 0 to 1.5 wt%

Thereafter, the FTIR test results in Fig. 2 show that the nitrile group on Spectra (a) to (e). Spectrum (a) shows the nitrile group at wave number $2,242.89\text{ cm}^{-1}$, the spectrum (b) at $2,242.81\text{ cm}^{-1}$, the spectrum (c) at $2,242.83\text{ cm}^{-1}$, the spectrum (d) at $2,242.79\text{ cm}^{-1}$ and spectrum (e) at $2,242.75\text{ cm}^{-1}$, respectively. The addition of styrene in the concentration ranging from 1.5 to 5% by weight causes the functional group of a benzene ring to occur in Spectra (c) and (d) at the wave number 705.41 cm^{-1} and 705.59 cm^{-1} , respectively, whereas the spectrum (e) occurs at 705.16 cm^{-1} and 763.71 cm^{-1} , respectively. In the previous work, Luo et al. reported in a functional group the benzene ring at the wave number $\sim 700\text{ cm}^{-1}$ and $\sim 760\text{ cm}^{-1}$, respectively, (P. Luo & Wu, 2012).

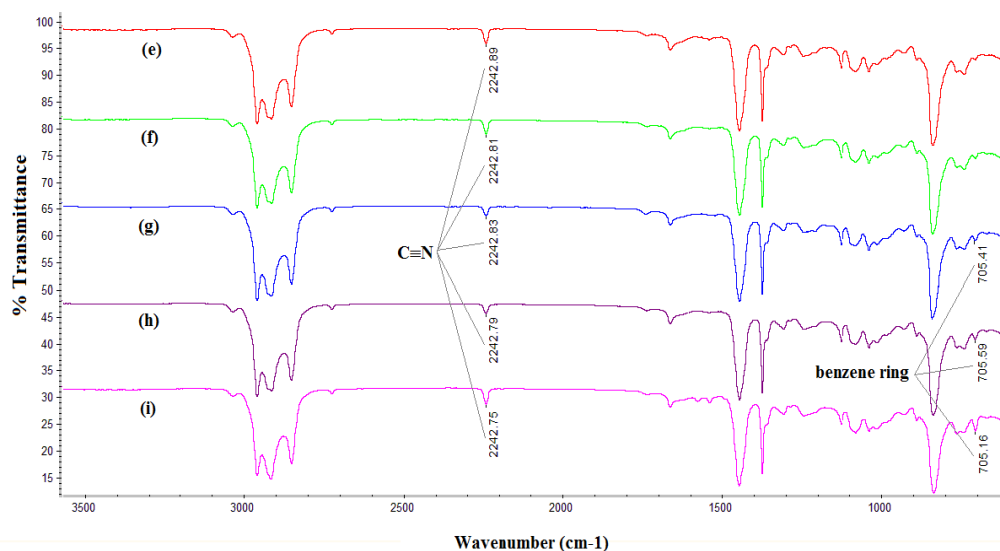


Fig. 2. FTIR spectra of copolymer with the addition of styrene range from 1.5 to 5 wt%

According to Myers, in general, coagulation is caused by the damage of the protein membrane because of the imbalance of positive and negative ions in the latex. The temperature rise in the system can induce collisions between sol particles and water molecules, therefore releasing electrolytes, which are absorbed on the colloidal surface

(Myers, 2003). Coincident with Myers' research, according to Chern, the viscosity of latex products increases with increasing temperature (up to 60 °C or even higher), therefore, it may display colloidal instability, (Chern, 2008).

In this case, the mixture's instability can be caused by an increase in temperature. Partial loss of electrolytes causes electrolyte imbalance and then coagulation of the latex. The addition of ST at certain concentrations makes the mixture stable enough to form products.

Increased viscosity also occurs due to the polymerization of AN to form polyacrylonitrile (PAN). Increased viscosity is related to a rate of the polymerization reaction of each monomer, (Rempp & Merrill, 1991). Acrylonitrile polymerization at 60°C has a value propagation constant of (k_p) = 2,000 mol⁻¹ s⁻¹; the termination constant is (k_t) = 1.6 x 10⁷ mol⁻¹ s⁻¹; an activation energy propagation is (E_p) = 3.9 kcal/mol, and the termination of activation energy is (E_t) = 3.7 kcal/mol. While styrene polymerization at the same temperature has a value of k_p = 145 mol⁻¹ s⁻¹ ; k_t = 5.8 x 10⁷ ; E_p = 7.3 kcal/mol ; E_t = 1.9 kcal/mol, respectively. From data of the polymerization reaction, polymerization of AN has a higher k_p value than the k_p value of ST and E_p . Additionally, the E_p AN is lower than E_p ST, causing an increase in the reaction rate between the radical monomers to the oligomers, which as a consequence, cause the rapid formation of polyacrylonitrile. The rapid rate of polyacrylonitrile formation causes increased viscosity, reducing the water content in the latex mixture. Hence, it results in coagulation of the mixture. The presence of styrene has a lower k_p value than the acrylonitrile. The styrene is the controller of the propagation reaction step for the acrylonitrile. The slowest reaction will control the total copolymerization reaction for the grafting. This is supported by Luo et al.'s statement that the stability of the colloidal system depends on the rate of reaction of the monomers, (Y. Luo, Xu, & Zhu, 2006).

According to Aldeeb, in the previous work, homopolymerization of acrylonitrile tends to decrease in the presence of the styrene monomer, therefore most of the uncopolymerized acrylonitrile monomer will start to decompose at the rapidly increased temperature, (Aldeeb, Rogers, & Mannan, 2003). This finding was confirmed by Kaur, et al., who stated that the presence of the styrene monomer could decrease the activity of the other monomer. This indicates that the two monomers, with electrons donated from the styrene monomer and other electron accepting abilities, enter into a charge transfer complex, therefore reducing the activity of the monomer towards grafting, (Kaur, Singh, & Gupta, 2005).

3.2. The Effect of the Ratio of DPNR to the Total Monomer (M) to the Styrene Addition

The influence of the ratio of DPNR to M with a variation between (60:40) and (70:30) wt% was observed. Table 2 shows that there was an increase in the concentration due to the addition of styrene when the ratio of DPNR to M was decreased. Part of the data in Table 2 was from Table 1. It can be explained that the ratio of DPNR to M decreased; the concentration of the total monomer increased; and variance in these ratios reacted simultaneously to form too many polymer particles, therefore increasing the viscosity in the mixture. The polymer particles cause the mixture to become viscous, to become unstable, and then cause coagulation of the latex. According to Chern, the tendency for unstable polymer particles, with a relatively high density compared to water, to undergo

coagulation and then sedimentation is greatly increased, (Chern, 2008). Thus, the greater the total monomer concentration needs to be, the greater the ST concentration needs to be to stabilize the graft copolymerization. Product characteristics were analyzed by FTIR. Fig. 3 shows that functional group of $C\equiv N$ on Spectrum (e) at wave number $2,242.89\text{ cm}^{-1}$ and on Spectrum (j) at $2,242.43$ and $2,361.93\text{ cm}^{-1}$, respectively. The difference of Spectra (e) and (j) was the presence of the benzene functional group on the Spectrum (j) at wave number 763.37 and 703.86 cm^{-1} , respectively.

| Table 2. The condition of process by ratio of DPNR to M | | | |
|---|---------------|-------|--------------------------|
| No. Spectra | Concentration | | Condition of process |
| | AN (%) | S (%) | |
| Ratio of DPNR to M = 70 : 30 wt% | | | |
| e | 100 | 0 | Coagulation before 1 h |
| | 99.5 | 0.5 | Coagulation after 1 h |
| | 99 | 1 | Coagulation after 2 h |
| | 98.5 | 1.5 | No coagulation until 6 h |
| Ratio of DPNR to M = 60 : 40 wt% | | | |
| j | 98.5 | 1.5 | Coagulation after 1 h |
| | 97.5 | 2.5 | Coagulation after 1 h |
| | 95 | 5 | Coagulation after 1 h |
| | 90 | 10 | No coagulation until 6 h |

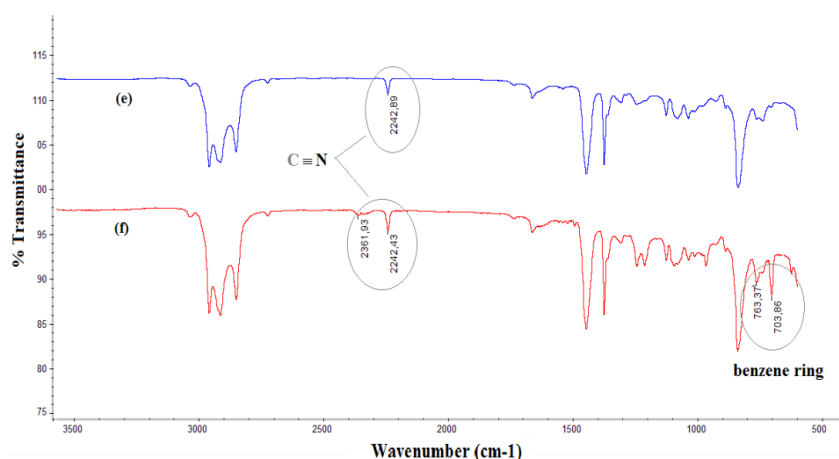


Fig. 3. FTIR spectra of copolymer with the ratio of DPNR to M with the variation of (60:40) and (70:30) wt%, respectively

From Tables 1 and 2 and the spectra in Figures 1, 2, and 3, the indications are that the presence of coagulation in the initial reaction did not lead to the formation of polyacrylonitrile in the mixture. The addition of styrene causes a reaction stability and prevents coagulation at the beginning of the reaction so as to form polyacrylonitrile in the solution.

3.3. The effect of reaction time

The reaction time has an important role in graft copolymerization as shown in Table 3. The graft copolymerization reaction time ranged from 5 – 10 hours.

Results of previous studies in Table 3 show that the graft copolymerization reaction of the acrylonitrile and styrene monomer takes at least 5 hours. This proves that in the event of coagulation in the early part of the reaction (1 – 2 hours in Tables 1 and 2) that copolymerization in the natural rubber latex has not occurred. This provides an explanation also to Figures 1b, 1c and 1d, since there is no functional group $C\equiv N$ that appears and this proves that there is no polyacrylonitrile bond onto natural rubber.

Table 3. Time of reaction in the previous works of the graft copolymerization of acrylonitrile and styrene onto natural rubber

| Monomer | Copolymerization method | Time of reaction | References |
|-------------------------------------|-------------------------|---------------------|--|
| Acrylonitrile & methyl methacrylate | Emulsion | 6 h | (Okieimen & Urhoghide, 2002) |
| Styrene | Emulsion | 10 h; 5 h; 8 h; 8 h | (Tho et al., 2002); (Suksawad et al., 2011); (Songsing, Vatanatham, & Hansupalak, 2013); (Sittiphan, Prasassarakich, & Poompradub, 2014) |
| Styrene & methyl methacrylate | Emulsion | 6 h; 8 h | (Man, Hashim, & Akil, 2008); (Kreua-Ongarjnukool, Pittayavinai, & Tuampoemsab, 2012) |
| Acrylonitrile & Styrene | Emulsion | 8 h | (Prasassarakich et al., 2001) |
| Acrylonitrile & Styrene | Solution | 6 h | (Angnanon et al., 2011) |

4. CONCLUSION

This study of graft copolymerization of acrylonitrile onto natural rubber, which is assisted by the styrene monomer in a semi batch reactor at a temperature of 65°C and at a pressure of 1 atm, resulted in several conclusions. : (i) the presence of the styrene monomer in the grafting reaction increases the stability process, (ii) the effect of the styrene monomer concentration on the emulsion stability is up to 1.5 wt% of the concentration of styrene at the ratio of deproteinized natural rubber (DPNR) to total monomer (M) of (70:30) wt%, (iii) the greater the total monomer concentration needs to be, the greater the styrene concentration needs to be to stabilize the graft copolymerization.

5. ACKNOWLEDGMENT

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October 01, 2015

Re: Acceptance Letter

Dear Tuti Indah Sari,

Greetings from Depok,

The editorial board is delighted to inform you that your paper entitled "The Effect Of Styrene Monomer In The Graft Copolymerization of Acrylonitrile Onto Deproteinized Natural Rubber" has been accepted to be published in the next issue of IJTech. At the present, we are conducting further necessary action to complete the publication process.

On behalf of IJTech, we appreciate your intention and willingness to publish your work with IJTech.

Warmest regards,



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