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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

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. Nagaty et al. (1980) observed differences in grafting acrylonitrile, ethyl acrylate and methyl methacrylate on insoluble starch. The case concluded that the reactivity order was AN > ethyl acrylate (EA) ≈ methyl methacrylate (MMA). Acrylonitrile is also a functional group

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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 et al., 2007). The presence of Polyacrylonitrile (PAN), as a homopolymer in the mixture will also increase the insolubility and resistance to organic solvents (Nataraj et al., 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 et al., 2014). In other works, the addition of ST onto isotactic polybutene-1 occurs, (Zhao et al., 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 et al., 2002), as well as for natural rubber (Angnanon et al., 2011; Prasassarakich et al., 2001), and for Chlorinated Polyethylene (CPE) (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^{o}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. EXPERIMENTAL PROCESS

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 ≥ 99%) and styrene monomer (ST ≥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 et al., 2008; Suksawad et al., 2011; Wongthong et al., 2013; Yamamoto et al., 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 et al., 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 $K_2S_2O_8$ 1 wt% as an initiator at a temperature of 65^oC. 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 0–5 wt % and the ratio of DPNR to M = 70:30 wt%

No. Spectra	Concentration		Condition of process
	AN %	ST %	
b	100	0.0	Coagulation before 1 h
c	99.5	0.5	Coagulation after 1 h
d	99.0	1.0	Coagulation after 2 h
e	98.5	1.5	No coagulation until 6 h
f	98.0	2.0	No coagulation until 6 h
g	97.5	2.5	No coagulation until 6 h
h	97.0	3.0	No coagulation until 6 h
i	95.0	5.0	No coagulation until 6 h

The characteristics of the product were investigated under FTIR analysis. FTIR test results in Figure 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 C≡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 (C≡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 et al., 2012). In previous work, a peak of C≡N could be found at 2,244 cm^{-1}, (Moafi et al., 2011).

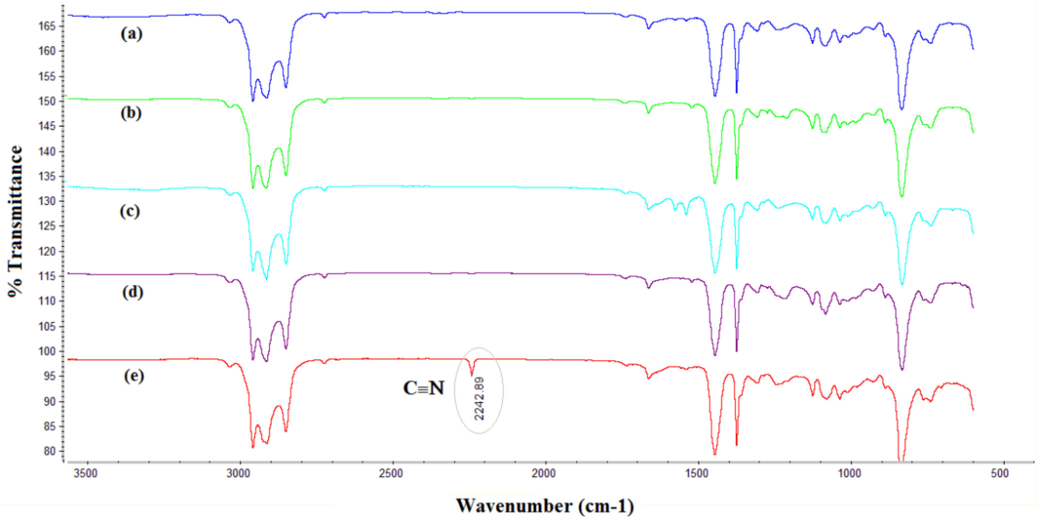

Figure 1 FTIR spectra of copolymer with the addition of styrene ranging from 0 to 1.5 wt%

Thereafter, the FTIR test results in Figure 2 show that the nitrile group on Spectra (a) to (e). Spectrum (a) shows the nitrile group at wave number 2,242.89 cm^{-1}, the spectrum (b) at 2,242.81 cm^{-1}, the spectrum (c) at 2,242.83 cm^{-1}, the spectrum (d) at 2,242.79 cm^{-1} and spectrum (e) at 2,242.75 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.

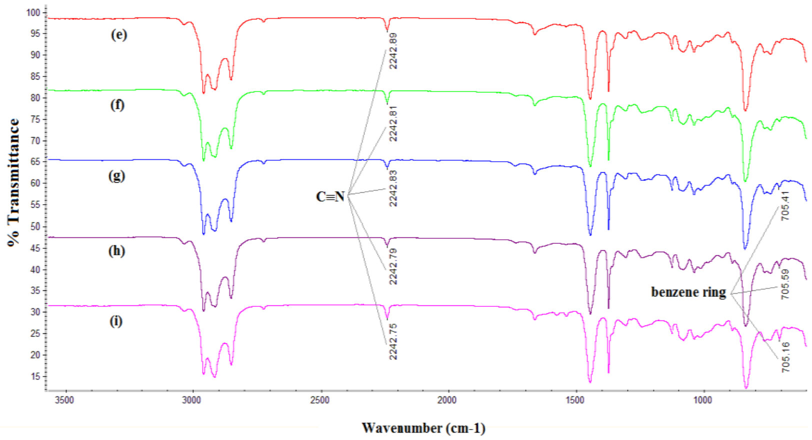

Figure 2 FTIR spectra of copolymer with the addition of styrene range from 1.5 to 5 wt%

In the previous work, (Luo & Wu, 2012) reported in a functional group the benzene ring at the wave number ~700 cm^{-1} and ~760 cm^{-1}, respectively.

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^{o}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^{o}C has a value propagation constant of (k_p) = 2,000 mol^{-1} s^{-1}; the termination constant is (k_t) = 1.6×10^7 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 10^7 ; 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 Ep. Additionally, the Ep AN is lower than Ep 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. (2006) statement that the stability of the colloidal system depends on the rate of reaction of the monomers,.

According to Aldeeb, in the previous work, homopolymerization of acrylonitrile tends to decrease in the presence of the styrene monomer, therefore most of the un-copolymerized acrylonitrile monomer will start to decompose at the rapidly increased temperature (Aldeeb et al., 2003). This finding was confirmed by Kaur et al. (2005) 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 et al., 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 (2008), the tendency for unstable polymer particles, with a relatively high density compared to water, to undergo coagulation and then sedimentation is greatly increased. 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. Figure 3 shows that functional group of C≡N on Spectrum (e) at wave number 2,242.89 cm^{-1} and on Spectrum (j) at 2,242.43 and 2,361.93 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. 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
	99.0	1.0	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
	95.0	5.0	Coagulation after 1 h
	90.0	10	No coagulation until 6 h

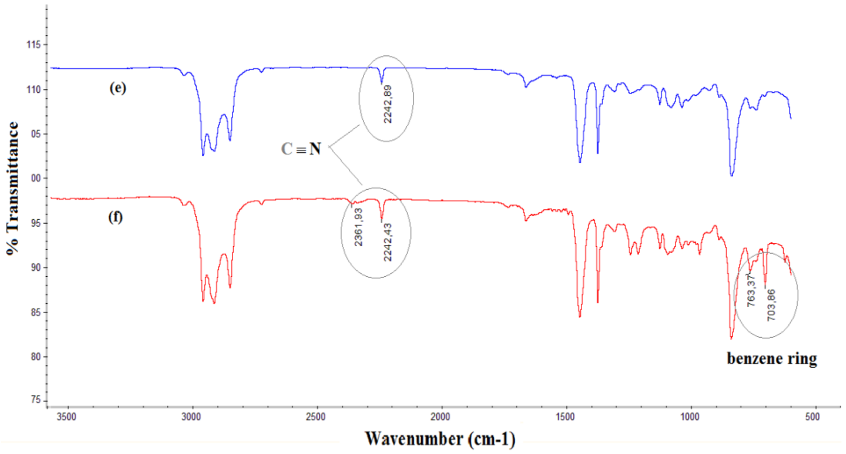

Figure 3 FTIR spectra of copolymer with the ratio of DPNR to M with the variation of (60:40) and (70:30) wt%, respectively

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≡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 et al., 2013; Sittiphan et al., 2014)
Styrene & methyl methacrylate	Emulsion	6 h; 8 h	(Man et al., 2008; Kreua-Ongarjnukool et al., 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%, and (iii) the greater the total monomer concentration needs to be, the greater the styrene concentration needs to be to stabilize the graft copolymerization.

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