

PRODUCTION OF NATURAL RUBBER GRAFTED STYRENE COPOLYMER LATEX AS WATER BASE COATINGS

Marga Utama¹ and Koentjahja Widjaja²

1. Center for The Application of Isotopes and Radiation Technology, National Nuclear Energy Agency (PATIR-BATAN) Jl. Cinere Pasar Jumat P.O.Box. 2 JKSKL, Jakarta 12070. Telp.(021) 7691907.

2. PT. Jaya Karya Utama, Jl. Let. Jen. S. Parman Kav. 107, Jakarta 11440.

ABSTRACT

PRODUCTION OF NATURAL RUBBER GRAFTED STYRENE COPOLYMER LATEX AS WATER BASE COATINGS. Twelve kinds formulation of natural rubber grafted copolymer styrene (NR-g-S) prepared by gamma radiation copolymerization technique has been carried out. The characteristic of NR-g-S and its water base coating such as molecular structure, particle size, and the properties of latex and its film were evaluated. The results showed that the NR-g-S latex as a water base coating has low viscosity, height strength, good grease resistance, good flexibility, good aging and corrosion resistance on concrete cement and metal. The average particle size is between 270-300 nm, and the bonding between poly-isoprene of NRL and styrene molecules were grafted copolymer.

Keywords: coating, water based, latex

INTRODUCTION

Water base coatings can be divided into three main classes : (a) aqueous dispersion or emulsions, (b) colloidal or water – solubility 4 dispersions, and (c) water reducible. The main differences characteristic among the three classes are the particle size and molecular weight such as : the particles size and molecular weight for emulsions are $> 0,1 \mu\text{m}$ and one million, but for solubility dispersions are 22-100 nm and 20.000 – 200.000, and for water reducible less then 20 nm, and 20 000 –50 000. [1].

The synthetic emulsion water base coating prepared by emulsion polymerization techniques available in the market are: styrene butadiene latex, butyl rubber latex, acrylate latex, butadiene acrylonitrile latex, vinyl acetate latex [2]. One of the drawbacks of that synthetic emulsion water base coating is emission of carcinogenic gas from catalyst such as nitrosamine. Some countries have imposed a restriction on the limit of emission for certain uses.

During the past 40 years ago, graft co-polymerization of natural rubber latex prepared by gamma radiation mainly for basic study related to their morphology, structure, etc. has been reported, but very few have reached industrial importance [3-6].

Two aspects graft co-polymerization of natural rubber latex as an adhesive are successively considered: first a more basic approach, to the behavior of pure, non accelerators vulcanizing agent, and second the process is more environment friendly [7-8].

According to the above data, this study is to production NR-g-S as water coatings. The hypotheses of this study is to prove that NR-g-S copolymers produced in pilot scale can be used as an aqueous dispersion or emulsions water base coatings with the quality satisfy the standard requirement.

EXPERIMENTAL

Material. Natural rubber latex with dry rubber content 60% obtained from Jalupang Rubber Plantation PTPN VIII Subang, Bandung. Styrene monomer obtained from PT.Gajah Tunggal Group Serang, and PT. Pardic Jaya. Jakarta.

Apparatus. Gamma Latex Irradiator with capacity 1,5 ton of emulsions water base coatings , Visconic Viscometer made in Tokyo Keiki Co. Ltd., and Infrared Spectrophotometer IR 435 Shimadzu.

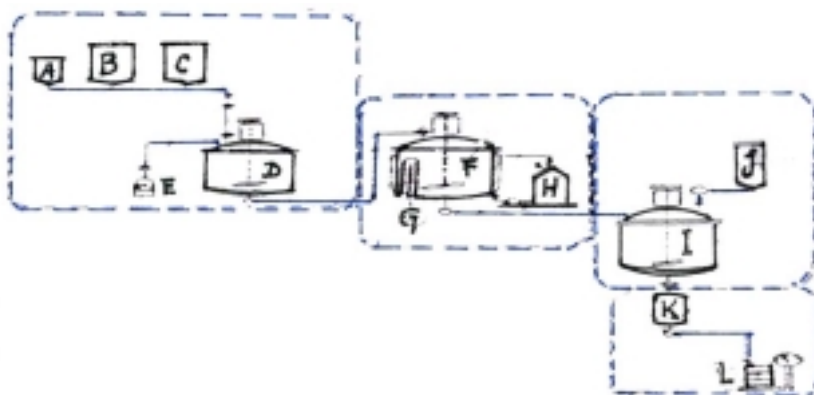


Figure 1. Flow diagram on the production of NR-g-PS prepared by gamma radiation co-polymerization of NRL technique as water base coatings.

Table 1. Three formulation for producing graft copolymer of natural rubber latex styrene prepared by radiation co- polymerization.

Chemical	Formulation		
	I	II	III
40% Natural Ruber Latex, phr	100	100	100
40%. Emulsion of styrene,phr.	25	50	100
20% Surfactant, %.	0.5	0.75	1.0
20% solution of KOH, phr.	1.0	1.0	1.0

Method. Two steps on the production of water base coatings emulsions prepared by gamma ray radiation co-polymerization technique namely production of NR-g-S, and production of water base coating emulsion are shown on Figure 1, with the details information are as follow:

Production of NR-g-S. Three type formulations of **NR-g-S** produced in this experiment (Table 1) with the procedure are as follow: Natural rubber latex with total solid content 60% after dilution to 40% from drum (A) introduces to the mixture vessel (D) by pump (E). The NR latex was mixed with 0.2 phr of 20% solution of KOH and 50% styrene emulsion from vessel (B) and (C) with concentration of styrene 25, 50, 100 phr. After completely, the mixtures were pumped into the reaction vessel (F) competed with cooling system (H), then irradiated by gamma ray (G) with variation irradiation dose of 15, 30, and 45 kGy. After irradiation the NRL-g-S was introduce into the mixing tank (I).

Production of emulsions water base coating. The NRL-g-S latex from mixing tank (I) is mixed by the 1% solution of KOH from tank (J) and 10% or 20% of talk powder. During addition of KOH and talc the micture should be stirred until the emulsion was homogeneous, then poured into the drum (L) through the filter (K).

Characterization of the NRL copolymer and it water base coating. The procedure for evaluation the character of NR-g-S and its water base coating such as molecular structure, particle size, properties of NR-g-S latex, and its water base coating were carried out according to the reference 9-11.

RESULT AND DISCUSSION

Industrial paints can be divided into several groups, depending on the end-uses such as application for finishes, automotive finishes, coil coating, coating for metal container, marine coating, air craft finishes etc. The detail information for the production of NRL-g-S latex prepared by gamma radiation co-polymerization of styrene into natural rubber latex, its emulsions water base coating, and its quality are as follows.

Production of NRL-g-S.

Radiation grafting of monomer into natural rubber can be carried out in a dry state and in an aqueous dispersion or emulsion. Radiation grafting in an aqueous dispersion or emulsion such in the latex form, has several advantages than in dry state, with the reason as follows:

1. Homogeneous distribution of monomer in rubber and homogeneous irradiation dose can be obtained easily.
2. Grafting reaction rate can be expected to be higher than that in dry state due to the influence of the free radical generated in water phase which diffuse to polymer particles.

with these intrinsic characteristic are rare, and one must resort to blends. However, cohesion in a two-component system is achieved only by chemical bonds between two macromolecules^[1]. The graft copolymer of NR-g-S not only chemical bonds between natural rubber and monomers but also chemical bond among monomers, so the advantage of graft copolymers are two structurally different type of polymer chains, such as: rigid polystyrene and rubbery natural rubber are associated in the same molecule.

A typical examples is given by system based on talc particle as the cohesive component, and NR-g-S particle as an adhesive component because this water base emulsions coatings contain talc with the particle size 50-100 μm as a seed particle, and the NR-g-S with particle size of around 0,1- 3μm (Figure 2), as a tacky agent.

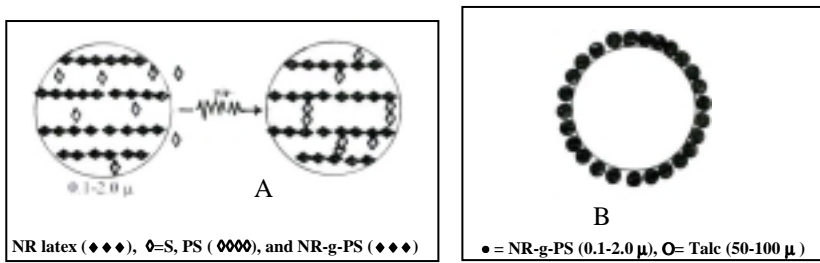


Figure 2. Typical illustration emulsion of NR-g-PS as water base coatings. A = illustration of radiation co-polymerization, B =Talc as a seed of particle and NR-g-S as tacky agent.

Table 3. The total solid content (TS) and viscosity(Vis.) of water base coatings with variation composition of NR-g-PS in talc, and concentration styrene content in NR-g-PS as a tacky agent. The irradiation dose absorbed of NR-g-PS is 30kGy.

Composition of NR-g-S in talc	Concentration of styrene in NR-g-S, phr.					
	25		50		100	
	TS, %.	Vis,c P	TS, %.	Vis,c P.	TS,%.	Vis,cP .
100 : 0	40	52	40	60	40	62
100 : 10	45	60	45	67	45	70
100 : 20	50	80	50	90	50	95

For industrial purpose it would be helpful to extend the high viscosity of the NR-g-S latex. Just as formulation usually added suitable tacky agent to impact the better viscosity to a given emulsions water base coating. Table 3 shows the adding effect of NR-g-S latex as tacky agent and talc as a seed of

particle on the viscosity of emulsions water base coating. It indicates that by adding the tacky agent, the viscosity of NR-g-S emulsion coatings increases.

Based on the results research application of the viscosity value coatings in this study, it can be recommended that the viscosity for producing emulsions water base coating is around 90-100 cP.

The main additive used for emulsions water base coating are resin (NR-g-S), solvents (water), filler, (talc) and stabilizer (KOH). Usually several different additives are incorporated into the NR grafted copolymers latex. They are chosen to be compatible with one of the phases rather than with both at once. Except for the filler and stabilizers, the solubility parameter of the additive gives a first indication of whether the letter is compatible with the PS, or NR latex.

3. Quality

The importance parameters for identify the quality of adhesive are : molecule structure, particle size, properties of latex and its film properties.

Molecule structure

Two kinds parameters namely infra red and NMR spectra for identification of NR-g-S as water base coating will be discussed in this topic.

Infra Red spectrum. Figure 3 shows the IR spectrum of NR, the mixture of NRL + styrene, and NR-g-S. This spectra prepared by Shimadzu Infra Red Spectrophotometer IR-435. It indicates that the spectrum of NR and the mixture of NR + styrene are quite the same. It means that the reaction between natural rubber and styrene is not occur, may be styrene was vapor during making a film. The specific finger print spectrum of NR is on the

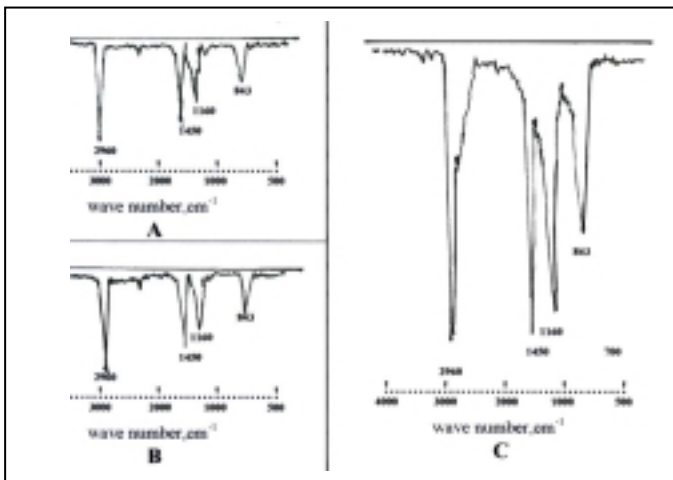


Figure 3. The IR spectra of NRL (A), the mixture of NR and styrene (B), and NR-g-PS film (C).

wave number 2900, 1450, 1375, and **843** cm^{-1} . The specific finger print spectrum of NR-g-S is on the wave number; 2960, **1660**, 1450, 1375, **843**, 840, and **700** cm^{-1} . From this data it can be concluded, that the specific spectra of NR-g-S is not only identified the quality of copolymer, but also can prove the bonding strength between poly-isoprene natural rubber and styrene is chemical bonding which is called graft-copolymer.

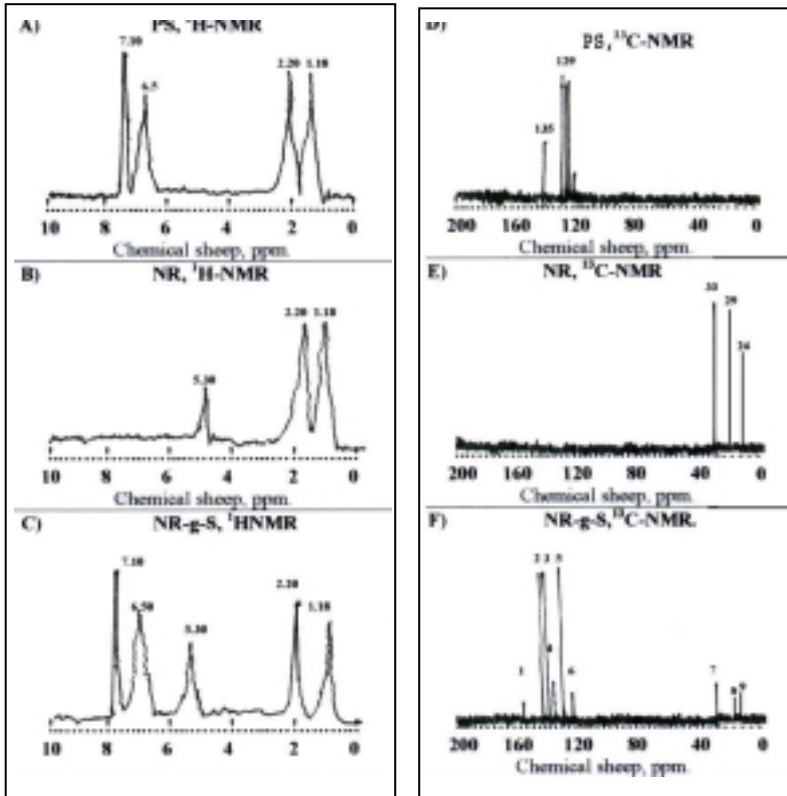


Figure 4. 90-MHz ^1H -NMR of poly-styrene (A), natural rubber (B), NR-g-S (C) and ^{13}C -NMR of of PS (D), NR (E), and NR-g-S (F).







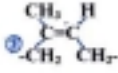
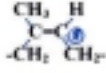
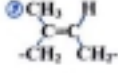
NMR Spectrum

Both ^1H -NMR and ^{13}C -NMR spectra taken at 89 MHz a JEOL FX-90 Q Fourier transform NMR Spectrometer of PS, NR, and NR-g-S is shown on Figure 4. The interpretation of NR and NR-g-S are as follow^[15,16]; the signal at 6.5 and 7.1 ppm of ^1H -NMR (Figure 4A) are attributed to the phenyl group of PS. The spectra of ^1H -NMR (Figure 4B) shows that the peak observed at 1.8 ppm is attributed the CH_3 group of poly-isoprene NR. The signal at 2.2 is attributed to the $-\text{CH}_2$, and the signal at 5.3 is attributed to the $=\text{CH}$ of poly-isoprene natural rubber. Figure 4C Shows that the five spectra of ^1H -NMR shows the combined signal of PS and NR-g-S.

Further information on the structure is provided by analysis of ^{13}C -NMR spectra of the PS, NR, and NR-g-S. Figure 4D-F show the ^{13}C -NMR spectra of PS, NR, and NR-g-S. The assignment of the spectra are listed on Table 5. From the table shows that the six signals at 135.4 – 125.7 are due to the phenyl group of PS. The other three peaks are attributed to the $-\text{CH}_3$, $-\text{CH}_2$, and $=\text{CH}_2$ groups of poly-isoprene of NR.

From the results of ^1H -NMR and ^{13}C -NMR confirm that the dominant content of the film the emulsion are PS, NR, and NR-g-S.

Table 5. ^{13}C -NMR chemical shifts (ppm) of the NR-g-PS from Figure 4F.

Chemical shift, ppm.	Intensity	Peak number	Structure
135.356	2.2	1	
129.126	99.7	2	
128.027	97.5	3	
127.373	3.7	4	
126.968	100.0	5	
125.665	3.3	6	
32.699	2.7	7	
26.998	3.7	8	
23.740	3.5	9	

Particle size

There are many ways of “visually” looking at the surface or cross-section of a piece of rubber, with instruments ranging from a simple lens (10 times), through a light microscope (10-400 times), scanning electron microscope (20–300 000 times), to a transmission electron microscope (1000–1000 000 times). Similarly the different elements present may be identified and, within limits, quantified by such techniques as X-ray fluorescence (XRF), electron spectroscopy for chemical analysis (ESCA), and many others, new acronyms for which are appearing continually. Whilst all of these

have their place, some indeed providing information not obtainable by any other method, the scanning electron microscope (SEM).

The first true SEM was built by Von Ardenne in 1938, but it was not until the mid 1960s that instruments became commercially available and the technique could be considered to have arrived. Most current applications are biomedical, biological or metallurgical and there is still relatively little published on the application of SEM to copolymer of natural rubber analysis[17-18].

The principle of operation is simple, and consists of bombarding the sample with high-energy electron beam, after coating it with a conductive film less than 1 nm thick to prevent build-up of an electric charge, and monitoring the events which results there from. The two events of interest here are the injection of secondary electron, which are processed to provide a “visual” TV image.

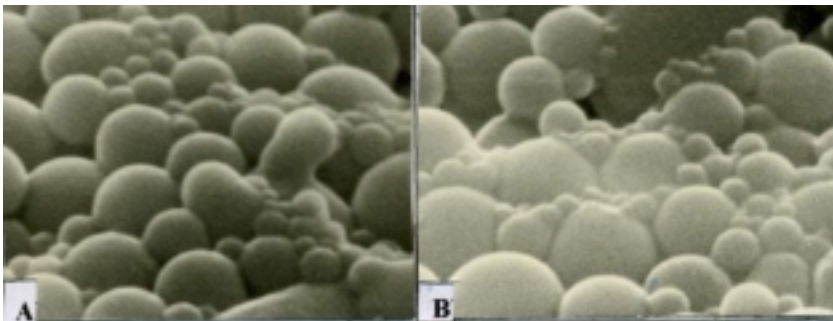


Figure 5. Electron micro-graph of NR (A) and NR-g-PS (B) after magnification 10.000 times.

It is a relatively simple matter to see the distribution latex, if they are hardened before drying with osmium tetroxide (OsO_4). Figure 5. shows that the difference distribution particle size between natural rubber latex and irradiated natural rubber latex particles is can not seeing, but by using a Nano Seizer apparatus, it was found that the average particles size of natural rubber is around 320 nm, and after radiation grafting of styrene into natural rubber with concentration of styrene 50 phr at 30 kGy, the particle average size increases becomes 360 nm. It means that after radiation co-polymerization processing, the rubber particle become swell, due to the cross-linking among poly-isoprene of NRL, grafting of styrene into rubber particles, an homopolymer of poly-styrene. It was also found that natural rubber particles form is an aggregate which consists of a number of particles, and the distribution of the particles diameter are around 0.1 – 2.0 μ .

Table 5. The properties of latex of NR-g-S latex and its film with different styrene content.

Treatment and properties	NR-g-S latex		
	I	II	III
Treatment			
• Concentration of. Styrene, %.	33	43	50
• Irradiation dose, kGy.	30	30	30
Latex properties.			
• pH	10.8	10.7	10.5
• Total solid, %.	48,8	48,7	49,1
• Viscosity, cP.	16	17	19
Film properties .			
• Modulus 300%, MPa.	3.0	4.1	5.2
• Tensile strength, MPa.	12.1	14.0	13.0
• Elongation at break, %.	800	750	700
• Hardness, Shore A.	60	67	75
Bonding strength for,			
• Play wood*, kg/cm ² .	7.8	8.9	9.7
• Particle board*, kg/cm ² .	9.7	9.8	9.9
• Wood Join, kg/cm ² .	4.3	4.2	3.8
• Canvas shoes**, N/6mm.	10	10	9.8
• Can sealing, kg/cm ² .	5	6	5

Note: * SNI;01-2704-1992 minimum 7kg/cm², ** SNI; 12-072-1987 minimum value 10/6mm, Formulation : I,II,&III are shown on Table 1 with irradiation dose 30 kGy.

Table 6. The properties of film on the can and concrete after out-door application of can-sealing coating, and concrete cement coatings in 50% KOH and 35% HCl during six months.

Properties	Out door application test during 6 months								
	Can sealing coating.			Concrete cement coating					
	On the top of building			In 50% KOH			In 35% HCl		
	I	II	III	I	II	III	I	II	III
1. Color change	G	G	G	G	G	G	G	G	G
2. Checking	G	G	G	G	G	G	G	G	G
3. Cracking	G	G	F	G	G	G	G	G	G
4. Alligatoring	F	G	G	G	G	G	G	G	G
5. Mud cracking	G	G	F	G	G	G	G	G	G
6. Wrinkling	G	G	G	G	G	G	G	G	F
7. Blistering	F	G	G	F	G	G	G	G	G
8. Microorganism.	G	G	G	G	G	G	G	G	G
9. Erosion	G	G	G	G	G	G	G	G	G
10. Peeling	G	G	G	G	G	G	G	G	G
11. Flaking	G	G	G	G	G	G	G	G	G
12. Undercutting	G	G	G	G	G	G	G	G	G
13. Pinhole	G	G	G	G	G	G	G	G	G
14. Holiday.	G	G	G	G	G	G	G	G	G
15. Bleeding.	G	G	G	G	G	G	G	G	G
16. Runs	G	G	G	G	G	G	G	G	G
17. Rusting	G	G	G	G	G	G	G	G	G

Formulation NR-g-S Type I, II and III are shown on Table 1 with irradiation dose 30 kGy and contain of talc is 20% w/w. G = good = no change compared with storage 0 month , F = fair.

The properties of latex and its film

The importance properties for adhesive which has been tested is shown on Table 6. It indicates that by increasing the polymer loading, the viscosity of latex, modulus, and hardness of film increase, while the maximum tensile strength and adhesive strength for play wood, particle board, and sealing compound were obtained on Type II. Based from these data it can be recommended that NR-g-S Type II can be able for play-wood, particle board adhesive, or can sealing compound.

The effect of out-door application of can coating-application and concrete cement application failures commonly encountered in service on can during 6 months is shown on Table 6. It indicates that the formulation Type II is the best water base coatings, because the properties of film of NR-g-S on can coatings was not change during six months storage out-door application and concrete cement application against solution of 50% KOH and 35% HCl. It means that NR-g-S Type II is a good resistance against base and acid.

Table 7. Technical specification of emulsions water base coating from NR-g-PS latex.

Properties	Minimum	Maximum	Average
Latex			
1. Color.	White milk	White milk	White milk
2. Solid content, %.	49	51	50
3. Density, kg/l	1.0	1.1	1.05
3. Viscosity, cP.	85	95	90
4. Temperature storage, °C.	0	40	20-30
6. Solvent	water	water	water
7. Solubility in water.	limited	limited	limited
8. pH	10.0	10.8	10.4
Film			
1. Density, kg/m ³ .	0.9	0.9	0.9
2. Modulus 300%, MPa.	1.0	1.0	1.0
3. Tensile strength, MPa.	20	20	20
4. Elongation at break, %.	800	800	800
5. Hardness, shore A.	40	40	40
6. IC ₅₀ .	>10	>10	>10
7. Toxicity	not toxic	not toxic	not toxic
8. Nitrosamin content ppb.	0	0	0
9. Allergy response	not allergy	not allergy	not allergy

Specification

The technical specification properties of NR-g-S as water base coatings is shown on Table 7. It can be seen that the coating not only have satisfy the standard requirement, but also free from carcinogenic chemicals (formaldehyde gas emission, and nitrosamine) and protein allergen. The advantages of NR-g-S prepared by radiation technique are more environment friendly.

CONCLUSION

From this study it can be concluded that graft copolymer of natural rubber styrene (NRL-g-S) latex prepared by gamma radiation copolymerization technique has been carried out in pilot scale, and can be used for water base coatings.

The quality of NRL-g-S as water base coatings is satisfied for the coating on metal and cement concrete. The bonding strength was not only satisfied with the standard requirement but also free from carcinogenic chemicals such as nitrosamine which can cause cancer.

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