

Article

Properties of Emulsion Paints with Binders Based on Natural Latex Grafting Styrene and Methyl Methacrylate

Bahrudin Ibrahim ^{1,*} , Zuchra Helwani ¹ , Arya Wiranata ¹, Ivan Fadhilah ¹, Joni Miharyono ² and Nasruddin ³ 

¹ Chemical Engineering Department, University of Riau, Pekanbaru 28293, Indonesia

² Warna Indah Tirta Asia (WITA), Pekanbaru 28291, Indonesia

³ Research Center for Agroindustry, National Research and Innovation Agency (BRIN), Tangerang 15314, Indonesia

* Correspondence: bahrudin@lecturer.unri.ac.id

Abstract: Infrastructure developments in recent decades have led to increasing demand for high-performance paints for construction and decorative purposes. Emulsion paint is water-based paint that is commonly used for coating the internal and external surfaces of a building. The quality and performance of this emulsion paint are highly dependent on its constituent components, such as binders, pigment, solvents, and additives. Emulsion paints initially used conventional formaldehyde-based binders and were, for some reason, prohibited from being used in paints due to health and environmental issues. The development of bio-based paints with natural rubber latex (NRL) has the potential to be developed as an emulsion paint binder. The results showed that NRL grafting of styrene monomer or MMA showed much better resistance to wet scrub and abrasion than PVAc at a monomer concentration of 20%, for styrene, and 30%, for MMA, with washability values reaching each of 11 and 12 cycles at 4% binder concentration. The NgSt20-4 and NgMMA30-4 binders' abilities to overcome wet scrub and abrasion increased with increasing paint binder concentrations, reaching 22 and 23 cycles at 10% binder concentration. Overall, the combination of NRL grafted with MMA monomer and 30% PVAc showed better performance and could compete with commercial binders such as PVAc. Adding methyl methacrylate monomer increases the adhesion and cohesion properties of the binder and increases the binder's resistance to scrubbing and wet abrasion. However, the combination of NRL grafted MMA and 30% PVAc showed the same effectiveness as NRL grafted MMA without PVAc, with more economical production costs.

Keywords: emulsion paint; grafting; methyl methacrylate; natural rubber latex; styrene



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1. Introduction

The development of infrastructure and buildings in the last few decades has been very fast, and is directly proportional to the increasing need for paint as a coating. Paint is used as a coating to protect the building from an object and as an interior or exterior decoration. Paint can provide a high aesthetic value to the building, making it a livable building [1–3]. Paints as coatings can be classified into three main categories: architectural or construction coatings, product or equipment coatings, and coatings with special purposes, such as preventing corrosion. Of the three main categories, emulsion paint is included in the first category [2].

Emulsion paint is water-based paint that coats the internal and external surfaces of a building. The quality and performance of emulsion paints are highly dependent on their constituent components, such as binders, pigment solvents, and additives [2,4,5]. The binder in paint plays an important role in attaching the pigment to the surface of the object being painted and becoming a continuous film. The type and amount of binder used in paint affects performance factors such as durability, stain resistance, adhesion,

and crack resistance. In general, the higher the ratio of binder to pigment, the higher the paint quality [4,6,7]. Commonly used binders in emulsion paints are water-dispersed binders such as polyvinyl acetate (PVAc) and styrene acrylic, known in the paint industry as synthetic latex [2,8].

PVAc-based binders are commercial adhesives that are widely used in emulsion paints. PVAc was chosen as the binder considering the nature of the PVAc material, which easily disperses in water, forms thin and colorless films, has good resistance to weathering and biodegradation, good initial adhesion, and low production costs [9,10]. The use of PVAc in some cases causes allergic reactions due to the formaldehyde content contained in these products [8,11,12]. This has attracted several studies to develop binders for emulsion-based paints that are environmentally friendly, non-toxic, have high adhesive properties, and have low cost. One of the potential materials that can replace PVAc is a natural polymer-based binder. Natural polymer-based binders are believed to be a solution to replace synthetic latex, such as PVAc, as emulsion paint binders.

Natural polymer-based binders have adhesive physical properties that are quite competitive with PVAc. There are significant differences between natural polymers and PVAc; the film formed by natural polymers is more elastic. Natural polymers have been widely applied to various types of paint, including gum arabic, turpentine, starch, protein, drying oil, beeswax, and natural latex [2,13,14]. One of the uses of natural polymers as raw material for emulsion paint binders is gum arabic, produced by *Acacia Senegal*. Gum arabic is generally used as a binder in watercolors because it is easily soluble in water. The use of gum arabic as a paint binder has the disadvantage of strong hydrocolloid properties, and makes the paint's drying time longer. Therefore, using gum arabic as a paint binder is more effective when mixed with PVAc. This is intended to improve the performance of gum arabic and reduce the use of PVAc as a paint binder with low cost [2,15,16].

In addition to gum arabic, natural rubber latex, better known as natural latex, produced by the *Hevea brasiliensis* plant, has the potential to be used as a binder or coating. This refers to the ability of natural latex to form a flexible film layer, which can coat a surface with a fairly good adhesive that is expected to reduce cracks in the emulsion paint [17]. The use of natural latex has challenges in its application. Natural latex has strong hydrocolloid properties, so it takes longer to dry [8,18]. Dry time is very important in the paint industry because it is related to the paint's resistance to water, the ability of the paint to adhere to the media, and the ability of the paint to bind to the substrate [8,14]. The use of natural latex as a binder in paint has the potential to be rapidly degraded when used for exterior coverage [19,20]. In addition, the content of several proteins in latex can cause allergic reactions in some people [21].

Natural latex can be applied directly or indirectly as a binder for emulsion paints. However, it should be noted that direct use of natural latex is not recommended. This is because raw natural rubber latex only contains dry rubber content (DRC) ranging from 20 to 40% [22]. The use of raw natural latex as a binder for emulsion paints has many disadvantages in terms of water resistance, thermal resistance, degradation by ultraviolet (UV), bacterial fungi, thin film coating, and weak bonding power to media and substrates [8,19,20,23]. In addition, the protein content contained in raw natural rubber latex can cause allergies and other health problems [21]. The modifications needed to produce high-performance natural latex include adhesive properties, water resistance, and resistance to degradation, which can be applied to various media and meet specifications as an emulsion paint binder. Modifying natural latex can be performed in various ways, including prevulcanization of natural latex, monomer grafting in latex polymer chains (grafting), cyclization, depolymerization, deproteinization, hydrogenation, chlorination, epoxidation, polymerization, with a combination of natural materials, or by using latex with other polymers to improve the characteristics of natural latex. In addition, a combination of the previously mentioned methods can be used [24].

The concentration of latex and deproteinization of natural latex became the basic procedure before further modification of natural latex. Concentration and deproteinization

of natural latex are most commonly carried out by combining creaming and centrifugation methods. The combined combination of these processes produces natural latex with a DRC of up to 60% and can reduce protein by up to 90% [25–27]. Using natural rubber latex that has been concentrated (DRC up to 60%) and depolymerized, better known as liquid natural rubber (LNR), has a relatively poor performance when applied as an emulsion paint binder. The performance of LNR as an emulsion paint binder is still unable to compete with the use of PVAc binders in terms of water resistance and paint dry time. The film's properties formed from using LNR binders tend to be flexible with weak adhesive properties. This makes the LNR not good enough to adhere to the media and bind to the substrate [8,22,28].

Modifying natural latex by grafting or substituting monomers in polymer chains opens up new opportunities to apply latex as a binder for emulsion paints. The splicing aims to improve the adhesive properties of natural latex and its water resistance. Styrene monomer and methyl methacrylate (MMA) implanted in the LNR improved the performance of the LNR. The use of LNR as an emulsion paint binder produces paint resistance to wet scrub and abrasion, better known as washability resistance, which produces a value of four cycles. Meanwhile, LNR grafted with a combination of styrene monomer and MMA increased the washability resistance of the emulsion paint up to 6–8 cycles at the same binder concentration of 4%. It is quite promising that LNR grafted with styrene monomer or MMA can improve LNR performance. However, the optimal combination of Styrene and MMA grafted onto LNR resulted in a binder that did not meet or could not compete with the PVAc binder. This is based on the fact that LNR grafted with a combination of styrene and MMA only produces emulsion paint with a washability resistance of 6–8 cycles. In comparison, PVAc based emulsion paint produces a washability resistance of up to 10 cycles [8]. Based on the review and evaluation of several studies, grafting of natural latex styrene and MMA is possible to improve the mechanical properties, including the adhesive and cohesive properties of the formed films [8,29,30]. The main obstacle to its application as a binder for emulsion paints is its water resistance is still very low. This makes grafted styrene and MMA latex films susceptible to swelling when exposed to water, and the binder loses its adhesive properties.

The poor water resistance of LNR grafted with styrene monomer or MMA can be minimized by combining it with a commercial binder such as PVAc. Natural rubber latex grafted with styrene or MMA showed high compatibility with PVAc, indicated by the absence of any indication of visual phase separation. The addition of a small amount of PVAc can improve adhesion, water resistance, and strong film coating, and delay the expansion of natural latex film splicing [28,30,31]. The main objective of this study was to optimize the performance of natural rubber latex grafted with styrene and grafted MMA as an emulsion paint binder by varying the concentration of monomer and combining it with a PVAc-based binder. Therefore, this research is expected to present natural latex as a green-based binder, reduce the use of PVAc-based binders, and meet applicable standards.

2. Materials and Methods

2.1. Material

The main material used is raw natural rubber latex produced by the people of Riau Province, Indonesia, with a dry rubber content (DRC) of 40–45% and technical specifications. Ammonia 45% sodium alginate, methyl methacrylate, and styrene monomer were purchased from PT Bratacho technical analyst specifications. Meanwhile, ingredients such as sodium dodecyl sulfate and potassium persulfate were purchased from Merck with pro-analyst specifications.

2.2. Method

The raw natural rubber latex obtained cannot be directly used as an emulsion paint binder. Therefore, that raw latex must go through several processing processes to become an emulsion paint binder, namely, pretreatment and concentration using creaming, grafting, and blending methods.

2.2.1. Preparation of Hight Ammonia Natural Rubber (HANR Latex)

Raw natural rubber latex is processed first before being further modified. Raw natural rubber latex needs to be treated to maintain the latex's stability in liquid form. Treatment is performed by adding a 45% ammonia solution to raw natural rubber latex with a concentration of 15% (*v/v*) as an anticoagulant. Raw natural rubber latex was measured for its dry rubber content (DRC) using the procedure according to SNI 06-2047-2002. This study recommends that the raw natural rubber latex has a DRC above 35%. It can increase the efficiency of the grating process in the next process.

2.2.2. HANR Modification of Latex with Polymerization Grafting

Improvement of latex HANR characteristics was carried out by modifying grafting monomer copolymerization. The monomers used were styrene (St) and methyl methacrylate (MMA) to increase the adhesion and water resistance of HANR latex. The HANR latex was fed into a 2 L batch reactor equipped with an agitator with a maximum speed of 500 rpm and equipped with a nozzle for connecting with nitrogen gas. Sodium dodecyl sulfonate (SDS) was added to a batch reactor containing 1% HANR latex. Nitrogen gas was flowed for 30 min before grafting to remove dissolved oxygen content in the latex. St and MMA monomers were added to the latex mixture with the formula shown in Table 1. The initiator used was 1.5 phr potassium persulfate. The grafting process lasted 6 h, then dissolved oxygen in the HANR latex was removed by flowing nitrogen gas into the batch reactor. After the grafting process, natural latex was further concentrated using creaming and centrifugation methods. The modified latex grafts are NRL-g-MMA, NRL-g-St, and NRL-g-St/NRL-g-MMA.

Table 1. Composition of Synthetic Materials NRL-g-ST and NRL-g-MMA.

Sample	NRL (%)	Styrene Monomer (%)	MMA Monomer (%)	Initiator (phr)
NRL-g-St	90	10	-	1.5
	85	15	-	
	80	20	-	
	75	25	-	
	70	30	-	
NRL-g-MMA	90	-	10	1.5
	85	-	15	
	80	-	20	
	75	-	25	
	70	-	30	

2.2.3. Latex Concentration Process with Creaming Method

Latex grafted styrene or MMA (NRL-g-St or MMA) was concentrated by creaming. The creaming process is carried out to separate components such as water, serum, and other rubber phase components in the latex. The creaming process was carried out by mixing a 3% sodium alginate solution with a ratio of 4 mL of sodium alginate solution to 25 mL of NRL-g-St. Furthermore, the NRL-g-St or MMA creaming process is accelerated by combining the creaming and centrifugation processes. The latex added with sodium alginate solution is centrifuged for one hour at 10,000 rpm. Then the latex, separated from other components such as water, serum, and other rubber components, is separated based on the difference in specific gravity. The final product is concentrated NRL-g-St or MMA with DRC levels ranging from 55 to 60%.

2.2.4. Emulsion Paint Manufacturing

The paint ingredients (Table 2) consist of four types: adhesives (binders), covering materials, color pigments, and preservatives. Ultramarine blue and caustic soda are included in emulsion paint color pigments. TiO₂, CaO, and CaCO₃ are covering materials

for emulsion paints. Polyvinyl acetate (PVAc) and natural latex are emulsion paint binders. Rochima is a paint preservative that maintains the mixing of the paint ingredients. The process of making the paint lasts 1 h, which is mixed sequentially, where the binder is mixed in the last stage of making the paint. The concentration of the mixed binder can be seen in Table 3. The resulting paint products were analyzed for the characteristics and suitability of the product for further development.

Table 2. Paint components, functions and grades.

Components	Utility	Manufacturer/Grade
Water	Dispersion medium	N/A
Hydroxyethyl cellulose	Thickening agent	Industrial
Caustic soda	Ph control	Industrial
Ultramarine blue	Blue pigment	Industrial
Alkylphenol ethoxylate	Surfactant	Industrial
TiO ₂	Opacity agent/White agent	Industrial
CaO	Hiding power agent	Industrial
CaCO ₃	Extender	Industrial
Polipropilen glycol	Anti-settling agent	Industrial
Eastment	Additive agent	Industrial
Dodecylbenzene sulfonat	Wetting agent	Industrial
NRL-g-MMA	Binder-1	
NRL-g-St	Binder-2	
NRL-g-(MMA-co-St)	Binder-3	
PVAc	Binder-4	Industrial

Key: N/A = Not available.

Table 3. Samples and Sample Codes Based on Variations in Binder Levels.

No	Sample	Sample Code	Binder (%)
1	PVAc	PVAc-4	4
2	PVAc	PVAc-6	6
3	PVAc	PVAc-8	8
4	PVAc	PVAc-10	10
5	Concentrated NRL	CNRL-4	4
6	Concentrated NRL	CNRL-6	6
7	Concentrated NRL	CNRL-8	8
8	Concentrated NRL	CNRL-10	10
9	NRL-g-10%St	NgSt10-4	4
10	NRL-g-15%St	NgSt15-4	4
11	NRL-g-20%St	NgSt20-4	4
12	NRL-g-25%St	NgSt25-4	4
13	NRL-g-30%St	NgSt30-4	4
14	NRL-g-10%MMA	NgMMA10-4	4
15	NRL-g-15%MMA	NgMMA15-4	4
16	NRL-g-20%MMA	NgMMA20-4	4
17	NRL-g-25%MMA	NgMMA25-4	4
18	NRL-g-30%MMA	NgMMA30-4	4
19	NRL-g-20%St	NgSt20-4	4
20	NRL-g-20%St	NgSt20-6	6
21	NRL-g-20%St	NgSt20-8	8
22	NRL-g-20%St	NgSt20-10	10
23	NRL-g-30%MMA	NgMMA30-4	4
24	NRL-g-30%MMA	NgMMA30-6	6
25	NRL-g-30%MMA	NgMMA30-8	8
26	NRL-g-30%MMA	NgMMA30-10	10
27	NRL-g-20%St/ NRL-g-30%MMA	NgSt/ NgMMA-4	4
28	NRL-g-20%St/ NRL-g-30%MMA	NgSt/ NgMMA-6	6

Table 3. Cont.

No	Sample	Sample Code	Binder (%)
29	NRL-g-20%St/ NRL-g-30%MMA	NgSt/NgMMA-8	8
30	NRL-g-20%St/ NRL-g-30%MMA	NgSt/NgMMA-10	10
31	NRL-g-20%St/PVAc (70/30)	NgSt20/PVAc-4	4
32	NRL-g-20%St/PVAc (70/30)	NgSt20/PVAc -6	6
33	NRL-g-20%St/PVAc (70/30)	NgSt20/PVAc -8	8
34	NRL-g-20%St/PVAc (70/30)	NgSt20/PVAc -10	10
35	NRL-g-30%MMA/PVAc (70/30)	NgMMA30/PVAc -4	4
36	NRL-g-30%MMA/PVAc (70/30)	NgMMA30/PVAc -6	6
37	NRL-g-30%MMA/PVAc (70/30)	NgMMA30/PVAc -8	8
38	NRL-g-30%MMA/PVAc (70/30)	NgMMA30/PVAc -10	10

2.3. Binder and Emulsion Paint Product Characteristics

Structural characteristics of the binder NRL, NRL-g-St, and NRL-g-MMA were analyzed using Fourier-transform infrared spectroscopy (FT-IR). Emulsion paint products were analyzed from the influence of the paint binder in general, namely water scrub resistance, opacity, and adjustable touch drying time. Set-to-touch drying (ASTM 1973) is a method for determining the drying rate of a paint sample layer painted on a substrate surface. The water resistance of the scrub was analyzed using a BGD 526 Wet Abrasion Scrub Tester. The opacity of emulsion paint was determined visually by passing and failing categories.

3. Results

3.1. Structural Characterization of the Graft Copolymer

Natural rubber latex (NRL) has unsaturated bonds where the unsaturated bonds determine the polarity, which is very important in determining the adhesion properties of a natural rubber material and its derivatives [17,32,33]. To be used as a binder with good adhesiveness, the polarity of NRL needs to be increased by grafting styrene (St) and methyl methacrylate (MMA) monomers in NRL. In addition, grafting certain monomers can also increase water resistance [8,32,34]. The grafting of monomers in a polymer chain can be viewed from the characterization of the polymer structure by looking at the FT-IR spectrum.

The FTIR spectrum in Figure 1 shows the FT-IR of natural rubber latex (NRL), natural rubber latex grafted with 30% MMA (NRL-g-MMA), and natural rubber latex grafted with 20% styrene (NRL-g-St). Natural rubber latex (NRL) has a distinctive peak shown in the absorption peak of 2957 cm^{-1} for C-H stretching, the absorption peak of 1637 cm^{-1} for the double bond in the polymer chain C=C stretching, and 1345 cm^{-1} for C-H bending from CH_3 deformation [35–37]. A similar observation was made on natural rubber latex grafted with 30% MMA (NRL-g-MMA). The analysis here focuses primarily on the prevalence of MMA grafted to NRL. New peaks indicating grafting were observed at 1721 and 1161 cm^{-1} absorption peaks of the NRL-g-MMA sample. These absorption peaks showed stretching C=O carbonyl groups and C-O-C stretching when MMA was grafted onto natural rubber side chains. The emergence of a new absorption peak accompanied by a decrease in absorption intensity at the peak of 1345 cm^{-1} proves the existence of an MMA segment on NRL-g-MMA. This is strong evidence to confirm the occurrence of a grafting reaction on NRL-g-MMA [34,36].

Meanwhile, in observations of natural rubber latex samples grafted with 20% Styrene (NRL-g-St), the same thing happened to the NRL-g-MMA samples. In the NRL-g-St sample, there was a decrease in absorption intensity at the peak of 1345 cm^{-1} for C-H bending from CH_3 deformation. A new absorption peak appeared at 1447 cm^{-1} , indicating C-H bending from the cyclo-hexane ring. This is evidence of styrene grafting onto NRL by replacing the CH_3 group in the natural rubber side chain. Therefore, based on the FT-IR spectrum in Figure 1, it can be concluded that styrene and methyl methacrylate (MMA)

monomers are proven to graft on natural rubber to form copolymers by replacing natural rubber side chains [37–39].

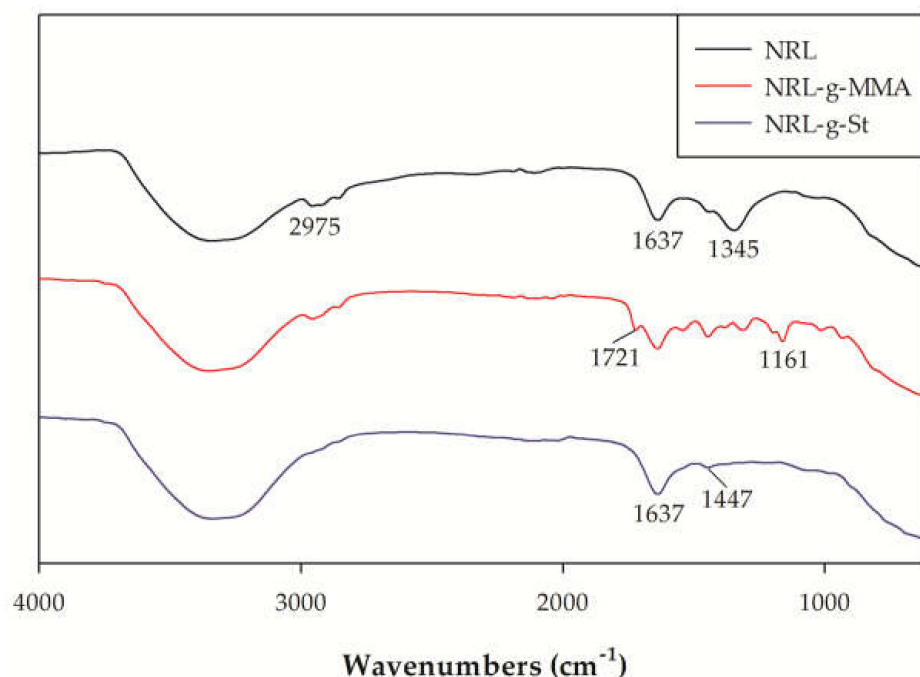


Figure 1. The FT–IR Spectra of NRL, NRL–g–MMA and NRL–g–St.

3.2. Washability (Wet Scrub Resistance)

Washability, or wet scrub resistance, is the ability of the paint film to resist scrubbing or wet abrasives without losing many paint components from the surface of the substrate. Washability was measured by counting the number of scrubbing and wet abrasive cycles until the entire paint film was finished or by measuring the weight loss of the coating after 1000 cycles [40,41]. The high or low number of wet scrub or abrasive cycles indicates the ability of the paint film to protect the substrate from dirt or abrasion by water. The ability of the paint film to protect the substrate from scrubbing or wet abrasives is influenced by the performance of binders and additives as a cover layer [40–42]. Based on the evaluations carried out in this study, the type and concentration of binders play an important role in film formation, such as adhesion, various optical and mechanical properties, and resistance to exposure to solvents or chemicals [14,43].

Figure 2 shows the paint washability of various binders, including commercial polyvinyl acetate (PVAc) based binders and modified and unmodified natural rubber latex (NRL). Commercial binder-based paints such as PVAc (sample PVAc-4) had the best washability (wet scrub resistance) at nine cycles for a binder concentration of 4%. In the paint based on the concentrated NRL of the binder (sample CNRL-4), the best washability values were obtained for only five cycles at the same binder concentration. CNRL-4 exhibits poor wet scrubbing and abrasion resistance. This is because NRL is a colloid that is not completely soluble in water, although it is inherently hydrophilic, which increases the sensitivity of NRL to water [8,44]. The high water sensitivity in the CNRL-4 sample is related to the mechanical properties of NRL, which have poor porosity because its adsorption properties are influenced by the amorphous molecular structure [45]. NRL has an unsaturated bond where the unsaturated bond determines the polarity, which is very important in determining the adhesion properties of a natural rubber material and its derivatives [17,32,33]. The combination of the concentrated NRL properties results in a binder with suboptimal performance. The film is formed flexibly, soft with adhesion, and has low scrub and wet abrasion resistance [32,46].

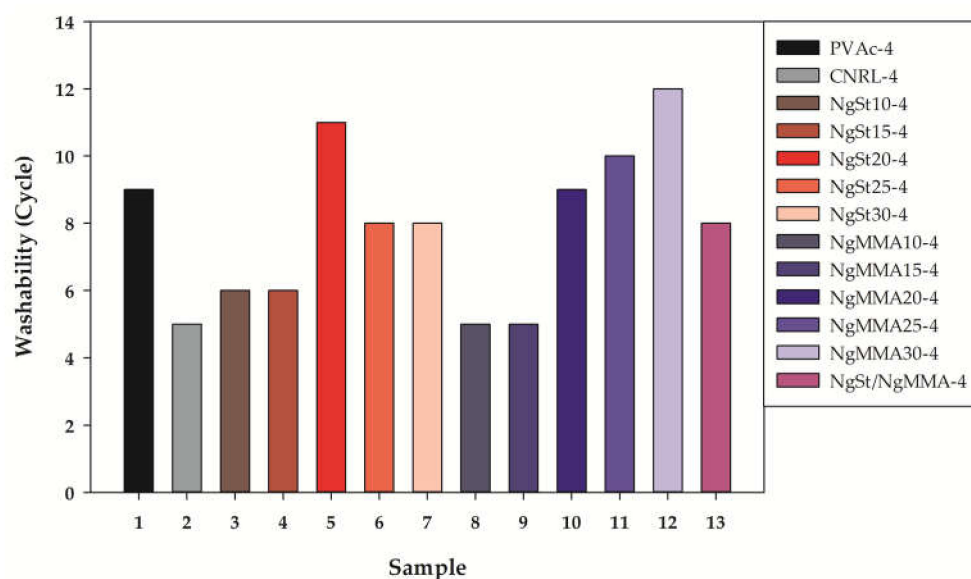


Figure 2. Washability of Various Types of Emulsion Paint Binders with Variations in Monomer Concentration.

The problem of using NRL as a binder can be overcome by grafting with polar materials, epoxidation, depolymerization to reduce the molecular weight of NRL, adding fillers, and combining NRL with synthetic polymers [8,32]. In this study, styrene (St) and methyl methacrylate (MMA) monomers were grafted in NRL. The purpose of grafting these monomers was to improve the adhesive properties of NRL through the formation of polarity sites. In addition, grafting certain monomers can also increase water resistance [8,32,34]. It can be seen in Figure 2 that NRL grafted styrene monomer (NRL-g-St) has increased the paint's resistance to wet rubbing and abrasion. The performance of NRL grafted with styrene reached the optimal point at the ratio of 20% styrene monomer (NRL-g-20%St) with a washability value of 11 cycles at the same binder concentration (Sample NgSt20-4). Grafting of more than 20% styrene monomer reduces the performance of NRL as a binder.

The grafting of more than 20% styrene monomer reduces grafting efficiency and allows not all monomers to be grafted onto the NRL polymer chain. This is because the increase in the number of monomers grafted also increases the energy to form NRL and styrene polymerization. Many possibilities will occur if the concentration of styrene increases. In addition to requiring more energy to form polymerization, increasing the concentration of styrene monomers increases the chances of forming styrene homopolymerization. In addition, the excess number of monomers in styrene limits the NRL active site to bind paint components and link them to the substrate [47,48].

In contrast to the styrene monomer grafted NRL, the methyl methacrylate (MMA) monomer grafted NRL (NRL-g-MMA) showed improved performance with frequent MMA ratio increases in NRL. The performance improvement of the NRL binder grafted with MMA began at a ratio of 20% MMA and reached its optimum at 30% MMA. The NRL sample grafted with 30% MMA (NRL-g-30%MMA) showed the best washability, reaching 12 cycles at the same binder concentration (sample NgMMA30-4). MMA grafted NRL is just as good as styrene. MMA promises much better performance on wet scrub and abrasion resistance. NRL grafted MMA promises better wet resistance, and grafted MMA in NRL polymer shows better compatibility with marked changes in hydrophilicity, increased adhesion, and film hardness. NRL grafted MMA monomer increases polarity and hydrophilicity, leading to high wettability resistance. In addition, the resulting film has a high adhesiveness and higher scrub resistance [34,36,49].

Another method was applied to improve the performance of NRL in terms of tackiness and water resistance. The method can change the hydrophilicity and polarity by mixing NRL-g-20% St and NRL-g-30% MMA with a ratio of 1:1 (Sample NgSt/NgMMA). The

results can be seen in Figure 2; there was an increase in washability, indicating that adhesion and water resistance increased. The overall performance of mixing NRL-g-St and NRL-g-MMA at a ratio of 1:1 was still below NRL-g-30%MMA and NRL-g-20%St at their respective optimum concentrations. The mixing of NRL-g-30%MMA and NRL-g-20%St could not achieve optimal performance, and a binding competition occurred between the radicals formed by styrene and MMA. The radicals formed in the MMA-grafted NRL were active in scavenging radicals apart from the styrene-grafted NRL. There is competition for the binding of radicals in the NRL chain, which affects the total number of radical sites, limits polarity, and makes the performance of the binder in binding paint components not optimal [47,50].

The performance of the binder is influenced by the concentration of the binder in the paint mixture. The increase in the concentration of the binder is directly proportional to the increase in the ability of the paint to overcome wet scrub and abrasion. It can be seen in Figure 3 that the washability of the emulsion paint increased along with the increase in the concentration of the binder, which was observed in all samples. Among all the samples presented, the concentrated NRL-based binder (CNRL sample) has the lowest performance compared to PVAc-based paint at various binder concentrations. Sample CNRL has a performance in overcoming wet scrub and abrasion only half of that of PVAc, indicating that the performance of concentrated NRL-based binders (CNRL sample) cannot compete with commercial binders such as PVAc.

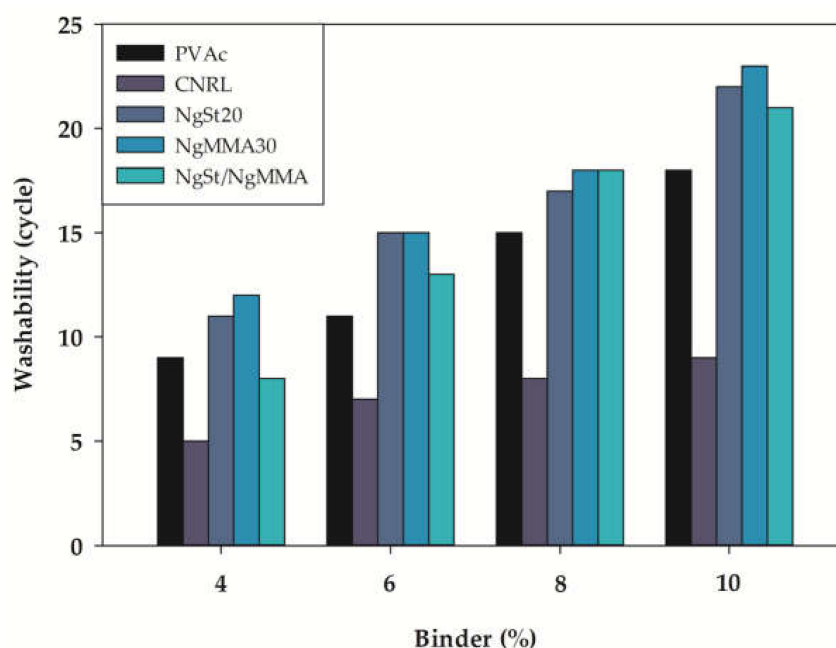


Figure 3. Washability of Various Types of NRL Binders at Various Concentrations.

Different things were observed in the NRL sample grafted with 20% styrene (sample NgSt20), the NRL grafted with 30% MMA (sample NgMMA30), and the combination of NRL grafted styrene and MMA (sample NgSt20/NgMMA30). As a result, all samples achieved optimal performance at 10% binder concentration, NgSt20-10 with 22 cycles, NgMMA30-10 with 23 cycles, and NgSt20/NgMMA30-10 with 21 cycles. Increasing the concentration of the binder in the paint mix not only increases the paint's resistance to wet rubbing and abrasion; increasing the binder concentration also improves adhesion, gloss, moisture resistance, weather resistance, and oil and solvent resistance [51,52]. Although the use of NRL-based binders grafted with styrene or MMA showed a very satisfactory paint performance, it should be noted that using NRL-based binders has a higher production cost. Therefore, combining NRL grafted with styrene or MMA with synthetic polymers should be considered to reduce production costs.

The combined performance of binders and synthetic polymers such as polyvinyl acetate (PVAc) shows that the binder's performance in paint film formation is very satisfactory. This is because monomer grafting can increase the adhesion and polarity of NRL, and PVAc shows high suitability and effectiveness in improving the mechanical properties of natural polymer-based materials, especially in terms of resistance to scrubbing and wet abrasion [18,32,53]. It can be seen in Figure 4 that the combination of NRL grafted with 20% styrene with PVAc at a ratio of 70:30 (NRL-g-20%St/PVAc) showed a significant decrease in binder performance at 10% binder concentration (Sample NgSt20/PVAc-10). The decrease in performance in the NgSt20/PVAc-10 sample may suggest a competitive radical binding reaction [30,47]. The styrene monomer radical site is very active in binding to the PVAc radical site, which reduces the radical site and decreases the adhesion to substrate binding. Further studies are needed to investigate the effect of mixing NRL grafted with styrene and PVAc on its polarity and hydrophilicity.

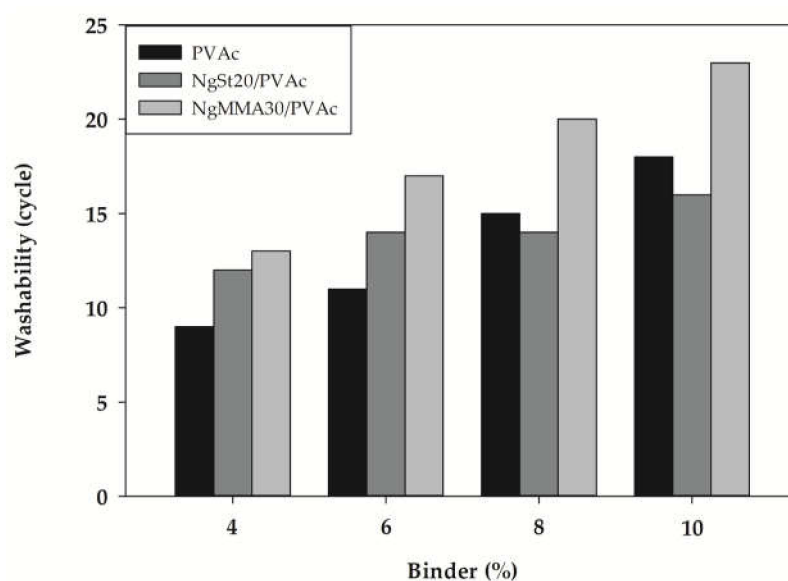


Figure 4. Washability Combination of NRL grafting Styrene or MMA and PVAc.

NRL grafted with 30% MMA combined with PVAc (NRL-g-30%MMA/PVAc) succeeded in increasing the paint binder resistance to scrubbing and wet sloughing much better than the combination of NRL-g-20%St/PVAc. As seen in Figure 4, the performance of the paint binder increased as the PVAc content increased, until it reached an optimal performance of 10% binder concentration, namely, the sample NgMMA30/PVAc-10 (23 cycles). Based on this, it can be concluded that PVAc plays an important role in increasing the resistance to wet scrub and abrasion while grafting MMA monomers in the NRL polymer chain improves adhesive properties, forms a film layer that is harder, more elastic, and has higher solvent resistance [8,10,53,54].

When comparing the performance of the combined NRL binder with styrene monomer or MMA and PVAc, the combined NRL with grafted MMA and PVAc monomer had significantly better performance. MMA monomer can polymerize with NRL faster than styrene and is more stable and non-solvent. MMA polymerized NRL is resistant to wet friction and abrasion [55]. The combination of NRL modification with monomer grafting and synthetic polymer blending has proven to be successful in covering the weaknesses and even increasing the performance of NRL-based binders as adhesives or binders. With the success of the modification of NRL as a paint binder, it is necessary to pay attention to the cost of producing paint when using a modified NRL-based binder. It is very important to use NRL as a paint binder.

3.3. Opacity

Opacity is the ability of a paint to remove or disguise the color of the substrate, and opacity is a function of the refractive index of the pigment, which is a numerical measurement of the ability of the pigment to bend light rays hitting its surface [55]. In this study, the pass and failed categories were used to measure the paint's opacity performance in disguising the substrate's color. The pass category is given to paints that can disguise the substrate color with just one brush, and the failed category is given to paints that cannot disguise the substrate color. In the paint composition used in this study, TiO_2 has the main role as an opacity former, while CaO and CaCO_3 act as hiding power agents and extenders. TiO_2 , CaO , and CaCO_3 combine to produce a white base paint with yellowing indications. At the same time, the sample using NRL as a binder has a clearer yellowing tendency which can be seen visually. Therefore, the addition of ultramarine blue pigment was applied to the paint to disguise yellowing indications and increase the paint's opacity.

Based on Table 4, the paint opacity in the failed category was found in the samples CNRL-4, NgSt10-4, NgSt15-4, NgMMA10-4, and NgMMA15-4. The five samples have the same binder content, namely 4%, binder concentration, and adhesive binder level, and play an important role in binding other paint components to form paint opacity, such as pigment, opacity agent, hiding power agent, and extender. Without the binder or with the low concentration of binder in the paint, some paint components that contribute to forming opacity will dissolve in the solvent and not optimally bind to the substrate. The same thing can happen if the adhesiveness of the binder decreases, where the polarity of the binder is so low that the paint cannot bind to other components and distribute them properly. Overall, the CNRL-4, NgSt10-4, NgSt15-4, NgMMA10-4, and NgMMA15-4 samples were NRL-based with lower adhesive and cohesive properties compared to commercial binders such as PVAc or a combination of NRL grafting monomer and PVAc. NRL is inherently hydrophilic with low polarity under high enough water content, so monomer-grafted NRL is expected to increase NRL's hydrophilic and polarity properties [8,34,36,44,49].

Grafting NRL above 20% styrene and 20% MMA showed good opacity at 4% binder content. This shows that the adhesiveness of NRL influences opacity as a binder. Increasing polarity forms an active site that binds the paint components that form opacity and connects them to form a film layer sufficient to disguise the color of the substrate. The paint opacity can be very good if the paint opacity agent (TiO_2 , CaO , and CaCO_3) is very well dispersed, free of aggregation, and the viscosity is not too high. TiO_2 , CaO , and CaCO_3 , in some cases, were found to cause agglomeration and aggregation in aqueous solution, which reduces the dispersion efficiency of these components in forming opacity [56,57]. Paint binders play an important role in regulating the dispersion of these components by forming a polymer composite. Composite polymers can be formed if only the binder adsorbs on the surface of the opaque agent. The challenge is precisely controlling the reactivity between the binder and opaque agent particles. If the reactivity is too slow, the binder will not adsorb onto the surface of the opacity-forming component. On the contrary, if the reactivity is too high, it will form aggregations [57].

The paint opacity results shown in Table 4 are directly proportional to the washability results shown in Figures 2–4, where samples CNRL-4, NgSt10-4, NgSt15-4, NgMMA10-4, and NgMMA15-4 have the lowest washability capabilities compared to other samples. This indicates that the three samples have poor adhesion and cohesion properties in binding paint components and substrates. The five samples showed very low scrub resistance, wet abrasion, and very low opacity. All samples using a binder combination of NRL and PVAc grafted monomer showed good opacity even though the binder content was low (4%). PVAc-based binders and their combination with monomer-grafted NRL exhibit excellent adhesion and cohesion to bond paint components and substrates. This allows the binder to form a composite polymer with much better opacity agents.

Table 4. Opacity and Drying Time of Emulsion Paints Based on NRL, NRL grafting Monomer and Combination with PVAc.

No	Sample Code	Binder (%)	Opacity (Failed/Pass)	Drying Time
1	PVAc-4	4	Passed	45.28
2	PVAc-6	6	Passed	58.33
3	PVAc-8	8	Passed	56.33
4	PVAc-10	10	Passed	60.45
5	CNRL-4	4	Failed	44.48
6	CNRL-6	6	Passed	48.24
7	CNRL-8	8	Passed	61.25
8	CNRL-10	10	Passed	75.15
9	NgSt10-4	4	Failed	49.15
10	NgSt15-4	4	Failed	52.34
11	NgSt20-4	4	Passed	55.30
12	NgSt25-4	4	Passed	56.32
13	NgSt30-4	4	Passed	58.34
14	NgMMA10-4	4	Failed	43.15
15	NgMMA15-4	4	Failed	47.10
16	NgMMA20-4	4	Passed	44.15
17	NgMMA25-4	4	Passed	48.23
18	NgMMA30-4	4	Passed	50.20
19	NgSt20-4	4	Passed	55.30
20	NgSt20-6	6	Passed	67.38
21	NgSt20-8	8	Passed	79.38
22	NgSt20-10	10	Passed	85.33
23	NgMMA30-4	4	Passed	44.15
24	NgMMA30-6	6	Passed	63.15
25	NgMMA30-8	8	Passed	72.33
26	NgMMA30-10	10	Passed	81.05
27	NgSt/NgMMA-4	4	Passed	48.38
28	NgSt/NgMMA-6	6	Passed	60.22
29	NgSt/NgMMA-8	8	Passed	71.34
30	NgSt/NgMMA-10	10	Passed	80.39
31	NgSt20/PVAc-4	4	Passed	50.44
32	NgSt20/PVAc-6	6	Passed	60.45
33	NgSt20/PVAc-8	8	Passed	75.30
34	NgSt20/PVAc-10	10	Passed	85.40
35	NgMMA30/PVAc-4	4	Passed	48.33
36	NgMMA30/PVAc-6	6	Passed	55.49
37	NgMMA30/PVAc-8	8	Passed	68.37
38	NgMMA30/PVAc-10	10	Passed	80.10

3.4. Drying Time

Drying time is the time it takes for paint to reach a certain level of dryness when touched, better known as set-to-touch time. In water-based paint applications, drying time becomes very important and is directly related to film formation. The faster the drying time, the lower the contamination of the paint layer to other components that can damage the paint layer [8,58]. Table 4 shows that at 4% binder content, PVAc-based binder paint has a drying time of 43–58 min and increases with increasing binder content in paint and monomer content. Styrene-grafted NRL samples require a longer drying time than MMA-grafted NRLs as the monomer concentration in NRL increases. This is attributed to the ability of the monomer solvent to evaporate, where the styrene monomer solvent takes longer to evaporate and form a film layer than the MMA monomer solvent. Likewise, with the combination of NRL grafting monomer and PVAc, where PVAc is an emulsion that is not completely soluble in water, increasing the binder concentration in the paint will require extra time to evaporate the water content and form a paint film fully.

Different things appear in the paint samples based on concentrated NRL and NRL grafted monomer combined with PVAc. Drying time is much faster than paint using NRL-based binder grafting monomer and its combination with PVAc. The short drying time indicates that the paint film formation process takes a very short time. This is possible for paints using NRL-based binders. NRL is a colloid not completely soluble in water, although it is inherently hydrophilic. NRL's simple molecular structure allows faster drying to form a paint film, even though NRL-based paints are not completely dry. The small amount of water in the NRL-based binder can reduce the adhesiveness of the paint, which prevents the film from sticking to the touch. This causes failure in measuring drying time using the set-to-touch time method.

Paint drying time is closely related to hydrophobicity, where NRL grafting styrene monomer or MMA shows changes in hydrophobicity. The hydrophobicity of NRL can be increased by combining NRL with polymers with high hydrophobicity, such as polyvinyl acetate (PVAc) [59]. From direct observation, paint samples using a combination of grafting monomer binder NRL and 30% PVAc showed almost the same drying time without PVAc. Further evaluation is needed to determine whether the monomer graft NRL-based binder and 30% PVAc exhibit sufficient dryness to form a film or failure of NRL adhesion.

4. Conclusions

Concentrated NRL-based binders cannot compete with synthetic polymer-based binders such as PVAc in terms of resistance to scrubbing and wet abrasion. The performance of paint samples using a concentrated NRL binder is only half that of PVAc in various binder levels. However, NRL grafting monomer styrene or MMA showed much better resistance to wet scrub and abrasion than PVAc at monomer concentrations of 20% for styrene (sample NgSt20-4) and 30% for MMA (sample NgMMA30-4) with respective washability values reaching 11 and 12 cycles at a binder concentration of 4%. NgSt20-4 and NgMMA30-4 binders' ability to overcome wet scrub and abrasion increased with increasing paint binder concentrations, reaching 22 and 23 cycles at 10% binder concentration.

Meanwhile, the combination of NRL grafted with styrene monomer (St) and methyl methacrylate (MMA) with 30% PVAc showed satisfactory performance. The combination of NRL grafted with monomer and PVAc showed the best washability performance. The combination sample of NRL grafted with monomer MMA and 30% PVAc (sample NgMMA30/PVAc-10) showed a value of 23 cycles at 10% binder content with a drying time of 80 min. Overall, the combination of NRL grafted with MMA monomer and 30% PVAc showed better performance and could compete with commercial binders such as PVAc. Adding methyl methacrylate monomer increases the adhesion and cohesion properties of the binder and increases the binder's resistance to scrubbing and wet abrasion. However, the combination of NRL grafted MMA and 30% PVAc showed the same effectiveness as NRL grafted MMA without PVAc, with a more economical production cost complex.

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