CHAPTER 2 LITERATURE REVIEWS

2.1 Polymer-modified mortar

Normally, polymer-modified mortar (PMM) is an ordinary mortar with added polymer in latex form, which the mix proportions of PMM are in the mass ratios of polymer to cement (P/C) in the range of 0.05 to 0.20, the cement to sand (C/S) in the range of 0.30-0.50, and the water to cement (W/C) in the range of 0.30-0.60 that depend on the required properties. In the present, PMM are used in applications such as paving and waterproofing materials, floorings, grouting wall and floor tile, patch and repair, and anticorrosive linings because the use of polymer latex in mortar usually improves the tensile and flexural strengths, adhesion, extensibility, and durability of the ordinary mortar by waterproofness and chemical resistance (Ohama & Ramachandran, 1996). For the improved flexural strength of PMM, Wang et al. (2016) give the physical model of PMM when the force in flexural mode is applied, as shown in Figure 2.1.

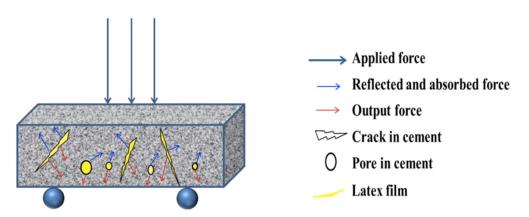


Figure 2.1 Physical model of PMM when the force in flexural mode is applied (Wang et al., 2016).

Figure 2.1 represents the polymer latex films and particles that absorb and reflect a part of the applied force during the flexural mode, improving the flexural strength of PMM. The polymer types that are used in mortar can be divided into two types as synthetic and natural polymers. Examples of synthetic polymers such as polyacrylate (PAE), styrene butyl acrylate (SBA), ethylene vinyl acetate (EVA), carboxylated styrene butadiene rubber (XSBR), styrene butadiene rubber (SBR), chloroprene rubber (CR), polyvinyl alcohol (PVA), etc. For the natural polymer as natural rubber (NR) (Ohama & Ramachandran, 1996; Zhang et al., 2021). The procedures for preparing the PMM currently have three methods, as shown in Figure 2.2. Figure 2.2a represents the mixture of water, admixture, and polymer latex directly added to the pre-mixed powders of cement and sand. Figure 2.2b represents the polymer latex added to the prepared fresh mortar. Figure 2.2c represents the preparation of water mixed with polymer latex and water mixed with mortar separately, then mixing these two mixtures together. However, there is no universal method for preparing the PMM. For a good mix, the method should be suitable for the type of polymer used in mortar (Zhang et al., 2021). The quality requirements for the PMM in JIS A 6203 are listed in Table 2.1.

Properties	Requirement
Flexural strength	Not less than 3.9 MPa
Compressive strength	Not less than 9.8 MPa
Adhesion	Not less than 0.98 MPa
Water absorption	Not more than 15%
Amount of water permeation	Not more than 30 g
Length change	0 to 0.15%

Table 2.1 Quality requirements of PMM in JIS A 6203.

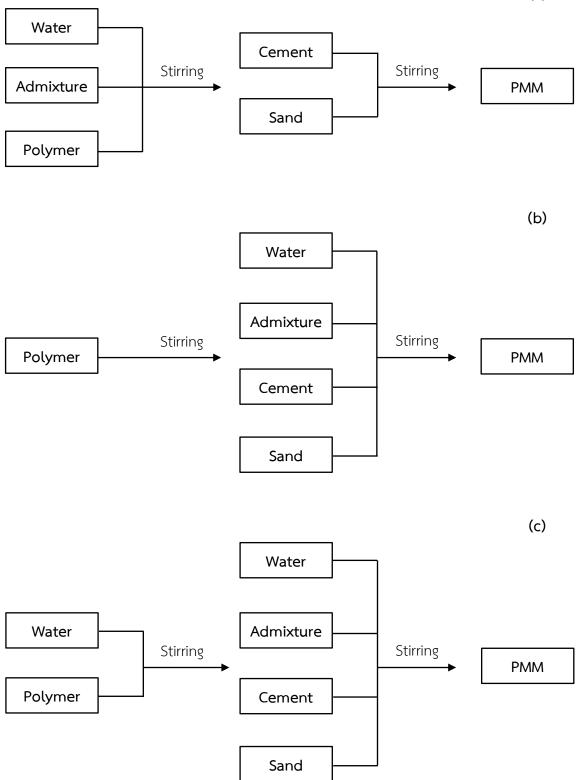


Figure 2.2 Schematic diagram of PMM preparation procedures.

(a)

2.2 Effect of the addition of polymer latex in mortar

2.2.1 Synthetic polymer

Knapen & Van Gemert (2015) reported the effects of addition of PVA in mortar at a P/C ratio of 0.01 on the compressive and flexural properties. For the mortar that cures in the water for 28 days, the result shows that the addition of PVA decreased the compressive strength of ordinary mortar because of air entrainment. However, the flexural strength of mortar added with PVA increased by more than 21% of the flexural strength value of ordinary mortar. This is because of the formation of PVA films in mortar.

Assaad (2018) reported the effects of additions of SBR and PVA in mortar at different contents on the compressive and flexural properties. When considered only the mortar that mixes by post-addition, fixes the ratio of W/C at 0.50, and cures for 28 days. The addition of SBR and PVA decreased the compressive strength of ordinary mortar. Because the addition of polymer in mortar retarded cement hydration, which increased porosity and weakened the mortar structure. While the flexural strength of mortar added with SBR and PVA increased with increasing the P/C ratio. This is because the polymer films can bridge the microcracks and reduce their propagation during the tensile loading. Moreover, considering the effects of different polymer types that were added in mortar at the same content on these properties, the result shows that all mortar with added SBR had a higher value than mortar with added PVA.

Wang et al. (2015) reported the effect of additions of SBR and styrene acrylic ester (SAE) in mortar at the P/C ratios of 0.01, 0.03, 0.05, 0.08, 0.10, 0.12, 0.15, 0.18, and 0.20 on the durability property in term of waterproofness. For the mortar that cures for 28 days, the water absorption resistance of mortar added with SBR and SAE increased with increasing the P/C ratio. For mortar added with SBR, the influence of increasing the P/C ratio on water absorption is not significant when the P/C ratio is more than 0.08. As the mortar is added with SAE, the influence of increasing the P/C ratio is not significant when the P/C ratio is more than 0.10. Thus, the optimal conditions on this property are the addition of SBR and SAE in mortar at the P/C ratios of 0.08 and 0.10, respectively.

Baghini et al. (2016) reported the effects of addition of XSBR in mortar at the XSBR contents of 0.05, 0.06, 0.07, 0.08, 0.09, and 0.10 on the mechanical properties. For the mortar that cures for 28 days, the unconfined compressive strength and abrasion resistance of mortar added with XSBR increased with increasing XSBR contents until it reached a XSBR content of 0.08. This is because both flexible butadiene chains and rigid styrene chains in the XSBR molecular structure provide good mechanical properties. However, the increment of XSBR content in mortar more than this content decreased these properties because the excess water from XSBR inhibited adequate mortar compaction.

2.2.2 Natural polymer

In the present, the natural polymer latex that is used in mortar has the only one as a natural rubber (NR). NR is a natural polymer that is obtained from the *Hevea brasiliensis* tree or Para rubber tree in latex form and consists mainly of two components are small particles of rubber and water. Additionally, some minor components such as proteins, lipids, carbohydrates, and inorganic components. Generally, the rubber particles in natural rubber latex (NRL) have spherical particles, which consist of 20 to 45% of the latex volume and are stabilized by the negative charge of surface surrounded by a mixed-layer of absorbed proteins and phospholipids. Currently, the possible model for NR particles has two models, as shown in Figure 2.3.

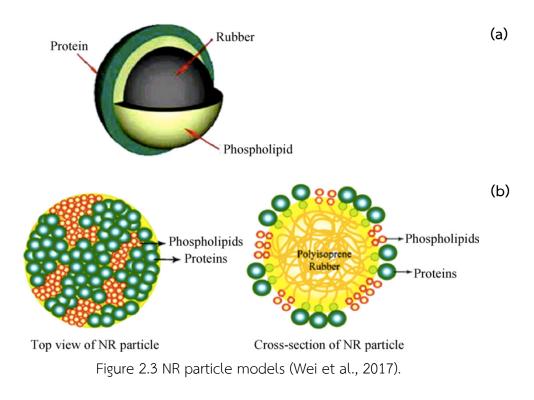


Figure 2.3a represents the NR particle surrounded by a double-layer of proteins and phospholipids and Figure 2.3b represents the NR particle surrounded by a mixed-layer of proteins and phospholipids (Nawamawat et al., 2011; Vo & Plank, 2018; Wei et al., 2017). The most chemical structure of NR is cis-1,4-polyisoprene, as shown in Figure 2.4.

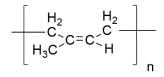


Figure 2.4 Chemical structure of cis-1,4-polyisoprene.

Currently, NR in latex and solid forms is used as raw material to produce the many products that cover several industries such as automotive, medical, and others. Examples of NR products include tires, belts, seals, gloves, tubes, etc. (Rajan et al., 2006). This is because it has high resilience, good tensile strength, good tear resistance, etc. (Chuayjuljit et al., 2015; Vu et al., 2015). However, to obtain the product properties as required, many NR products usually combine with other rubber, filler, or both. Several times, there is an issue with incompatibility between NR and combinations, requiring the use of additives in the system to improve the functionality of materials. The common fillers that are used in the rubber industry include carbon black, silica, calcium carbonate, clay, fiber, etc. (Abdul Salim et al., 2018; Wongsorat et al., 2014). In addition, the use of NR, especially in latex form is also found in the construction industry in its applications as a modifier in asphalt, concrete, and mortar.

Sukmak et al. (2020) studied the effects of addition content of NRL in paste at the P/C ratios of 0.10, 0.20, 0.30, 0.40, and 0.50 on the mechanical properties. All the pastes were fixed the ratios of W/C at 0.55 and SDS/P at 0.10, where the SDS is a sodium dodecyl sulfate that used to provide the stability of NR particles. Then it was cured at a controlled air temperature for 28 days before testing. The addition of NRL in paste was found to improve the flexural strength and toughness of ordinary paste. On the other hand, the compressive strength of paste with added NRL was found to decrease this property of ordinary paste. This is because of the retardation effect from the presence of NR films and air bubble pores. In this study, the addition content of NRL in paste at a P/C ratio of 0.10 is an optimal condition, which provides the highest compressive and flexural strengths of all the paste with added NRL.

Loykaew & Utara (2020) studied the effect of replacement content of cement by NRL at 3, 6, 9, and 12% by weight on the durability property of paste in the acid and sulfate environments. All the pastes were used with the SDS to improve the compatibility between NRL and cement. Then it was cured in water for 28 days before testing. Based on the result of compressive strength, the replacement content of cement by NRL at 12% by weight is optimal, which increases the stability of paste after acid and sulfate immersions. This is because the NR films can exhibit the diffusion of acid and sulfate that help join the cement components together. Moreover, when compared to the paste with replaced NRL at the same immersion time, the paste with replaced NRL showed greater resistance to sulfate than acid environments.

Yaowarat et al. (2021) studied the effects of addition of NRL in concrete at different contents on the compressive and flexural properties. Considering only the concrete, which fixes the ratio of W/C at 0.30 and cures for 28 days. The results show the compressive strength of concrete added with NRL decreased with increasing the P/C ratio. This is because the NR formed the thick films around the cement, which retarded its hydration. While the flexural strength of concrete added with NRL increased with the highest value was found in the P/C ratio at 0.58% by weight because the films enhanced the cohesion among the aggregate particles that improve the flexural strength of ordinary concrete. Moreover, this study suggested that this condition met the minimum requirements for compressive and flexural strengths for concrete pavement specified by the Department of Highways, Thailand.

However, the use of synthetic and natural polymers in latex form results in the same trend that enhances the tensile and flexural strength, extensibility, adhesion, and durability of ordinary mortar through waterproofness and chemical resistance. On the other hand, the compressive strength of most PMM is lower than ordinary mortar. To resolve this issue, the use of silica combined with polymer in mortar is an alternative way. This is because the use of silica in mortar usually improves the compressive strength of ordinary mortar by having a pore-filling effect (Aggarwal et al., 2015).

2.3 Effect of the addition of silica in mortar

Rupasinghe et al. (2017) reported the effect of replacement content of cement by nano-silica at 4, 8, and 12% by weight on the compressive property. The replacement of cement with nano-silica increased the compressive strength of ordinary paste. In this research, the optimal replacement content of cement by nano-silica was found at 8% by weight. As the replacement content of cement by nano-silica exceeds 8% by weight, the overall hydrated phase volume and the capillary pore volume of paste decrease and increase, respectively, which reduce the compressive strength.

Khan et al. (2020) reported the effects of micro-silica extracted from rice husk ash and used to replace cement in mortar at the contents of 5, 15, and 25% by weight on the compressive and flexural properties. For the mortar that cures in the air for 28 days, the replacement of cement by micro-silica increased the compressive and flexural strengths of ordinary mortar. In this research, the highest values of compressive and flexural strength were found in the replacement content of cement by micro-silica at 5% by weight. As the replacement of cement by micro-silica is more than this content, the micro-silica agglomerates and forms the weak point in mortar.

Jo et al. (2007) reported the effect of nano-silica and silica fume replacing cement in mortar at different contents on the compressive property. The result shows the compressive strength of all mortars replacing cement with nano-silica was higher than the mortars replacing cement with silica fume. Because the nano-silica is more effective in the pozzolanic reaction than the silica fume that fills the pores of ordinary mortar. In this research, the highest compressive strength was found in the replacement content of cement by nano-silica at 12% by weight with the value of 68.80 MPa after curing in water for 28 days.

According to the literature, the current silica used in mortar derives from both natural and synthetic extractions. In addition, the current silica used in mortar is found in nano- and micro-sized particles. When comparing the silica source and silica size, the literature reveals that the silica size is more important to mortar properties than the silica source. Currently, several industries, including the construction industry are focused on using local and natural materials from renewable resources to produce products with the required properties. Thus, the development of PMM to be more effective and sustainable with the use of materials from natural sources is an interesting approach. For example, the use of NRL combined with nano-silica extracted from natural sources. In the present, silica is extracted from several natural sources such as corn cob, sugarcane bagasse ash, bamboo, rice straw, rice husk ash, and others. The preparation of silica using rice husk ash (RHA) is an interesting approach because normally it contains a high silica content of over 60%. Furthermore, RHA is the byproduct of the process of rice husk (RH) pyrolysis for energy production, which is usually dumped in landfills, leading to air and water pollution. To reduce this issue and increase the value of this material, the current use of RHA is in many applications such as fertilizer, adsorbent and catalyst in the form of activated carbon or silica, and in the cement and concrete industries in the form of silicate or silica, etc. (Pode, 2016; Shen, 2017; Shen et al., 2014).

2.4 Preparation of silica from rice husk ash

There are several methods to extract silica from RHA, including heat, lye, solgel, and precipitation (Guo et al., 2021). The precipitation method is popular because it is simple, economical, and repeatable. To obtain silica, the main conventional procedure is to first extract it using alkali and then precipitate it using acid (Yuvakkumar et al., 2014).

Thuadaij & Nuntiya (2008) prepared the nano-silica from RHA by the precipitation method. First, the sodium hydroxide (NaOH) solution was used to extract silica from RHA for 3 hours. The solution was filtered to obtain the sodium silicate solution. The 5N sulfuric acid (H_2SO_4) was added to the sodium silicate solution until the pH reached 2, and then ammonium hydroxide (NH₄OH) was added to the previous solution until the pH reached 8.5. The solution was left for 3.5 hours. The pure silica was filtered from the previous solution and dried at 120° C for 12 hours. In this study, the optimal condition to prepare pure silica is to use RHA that has been calcined at 700°C for 6 hours as the raw material and a 2.5N NaOH solution to extract silica. Then, the pure silica was extracted by refluxing with 6N hydrochloric acid (HCl) for 4 hours and washing it with deionized (DI) water to make the acid free. The pure silica was dissolved in 2N NaOH solution by stirring for 10 hours, and then H₂SO₄ was added to adjust the pH of the solution in the range of 7.5-8.5. The nano-silica was washed with warm DI water to make it alkali free and dried at 50°C for 48 hours. The prepared nano-silica showed an agglomerate form with a diameter of about 50 nm and a specific area of 656 m^2/g . Moreover, the prepared nano-silica was found to have a typical amorphous form.

Majumder et al. (2014) prepared the amorphous silica from RHA by the precipitation method. First, the collected RH was sieved to remove dust, washed with DI water to remove impurities of soil and dust, and dried at 60°C for 24 hours. Then, the dried RH was calcined at 450°C for 15 minutes to obtain the RHA. The RHA was washed with DI water, dried in hot-air oven for 24 hours, and crushed to a size of 300 micrometers. Then, the RHA was washed with 2M HCl for 2 hours to remove mineral impurities and the residue of RHA was filtered. The filtered residue was washed with

DI water and dried at 60°C for 24 hours. Then, the silica was extracted from the previous RHA using a 1M NaOH solution at 80°C for 2 hours and filtered the residue of unreacted RHA to obtain the sodium silicate solution. Then, the sodium silicate solution was titrated with 2M HCl to adjust the pH of the solution in the range of 7-10 and aged for 24 hours to form silica gel. The DI water was added to silica gel and stirred to make a slurry solution. The slurry solution was centrifuged at 6,000 rpm for 15 minutes to obtain the separated solid gel, washed with DI water, and dried at 80°C for 12 hours to form with a silica. The prepared silica was found to have a typical amorphous form with a silica content greater than 90%.

Dhaneswara et al. (2020) prepared the silica from RHA by the precipitation method. The RHA was calcined at 700°C for 5 hours to obtain the RHA that is used as the raw material. The silica was extracted from RHA using 5% or 10% NaOH solution at 80° C for 1 hour and the residue of unreacted RHA was filtered out to obtain the sodium silicate solution. Then, the 1M HCl or acetic acid (CH₃COOH) was titrated into the sodium silicate solution to a pH of 7, which forms the silica gel. The previous gel was filtered and dried at 120°C for 12 hours. Then, the silica was washed with DI water at 80° C for 15 minutes to dissolve any salts that might form, filtered, and dried at 120°C for 4 hours. All the prepared silica was found to have a typical amorphous form with a purity of 98-99%. In this study, the silica extracted from 10% NaOH and precipitated using HCl had the largest surface area.

However, it is known that silica and NR are generally incompatible due to the polarity and non-polarity of materials. Thus, to improve the functionality of materials, using vinyltriethoxysilane (VTES) as a compatibilizer or XSBR combined in the systems may reduce this issue. The chemical structures of VTES and XSBR are shown in Figures 2.5 and 2.6, respectively.

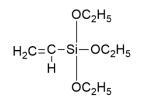


Figure 2.5 Chemical structure of VTES.

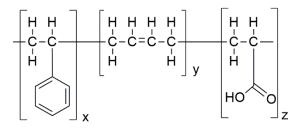


Figure 2.6 Chemical structure of XSBR.