

CHAPTER IV

METHODOLOGY

PERFORMANCE OF NATURAL RUBBER LATEX MODIFIED BOTTOM ASH-BASED GEOPOLYMER STABILIZED RECYCLED CONCRETE AGGREGATE AS A PAVEMENT SUBBASE MATERIAL

4.1 Introduction

Recently, geopolymers have gained prominence attention in the concrete industry, building material, road construction in pavement base/subbase layer, and several research studies have been conducted to address their short and long-term performances. Geopolymer is made of alkali-activated aluminosilicate materials such as FA, slag, rice husk ash, and bottom ash. Geopolymers are reported to produce low CO₂ emissions and energy consumption (Palomo, Grutzeck, & Blanco, 1999). These shortcomings have led to an attempt to explore novel low carbon stabilization methods. Geopolymer is an inorganic aluminosilicate material synthesized by alkaline activation of materials rich in alumina (Al₂O₃) and silica (SiO₂) and is considered as a green cementing agent. Geopolymerization involves the chemical reaction of aluminosilicate oxides by alkaline activation, yielding the polycondensation of the material in the three-dimensional silico-aluminate structure (Davidovits, 1991; Zhang, He, & Gambrell, 2010). Three typical structures of geopolymer are: Poly (sialate) type (-SiO-Al-O-), the Poly (sialatesiloxo) type (-Si-O-Al-O-Si-O-), and the Poly (sialate-disiloxo) type (-Si-O-Al-O-Si-O-Si-O-). Geopolymer has in recent years been used to stabilize natural soils to develop green building materials such as masonry products. It was reported that geopolymer based materials possess higher compressive strength and durability against sulfate than cement based materials (Sukmak, De Silva, Horpibulsuk, & Chindaprasirt, 2015; Sukmak, Horpibulsuk, & Shen, 2013; Sukmak, Horpibulsuk, Shen, Chindaprasirt, & Suksiripattanapong, 2013). Recently, (Suksiripattanapong, Horpibulsuk, Chanprasert, Sukmak, & Arulrajah, 2015) and (Horpibulsuk, Suksiripattanapong, Samingthong, Rachan, & Arulrajah, 2016) successfully stabilized water treatment sludge using fly ash based geopolymer to develop sustainable non-structural and bearing masonry units. It was illustrated that the geopolymer is more effective than PC in stabilizing the water treatment sludge with high alum content. The strength and

durability of sludge-geopolymer masonry units is significantly higher than sludge-cement masonry units.

Highway construction is an important aspect in infrastructure construction in many developed and developing countries. Highway construction however consumes a large amount of natural quality aggregates, particularly in their pavement base/subbase layers. As a result, the quarries and gravel pits are increasingly exploited as a source of pavement materials, which notably leads to subsequent devastating of natural environmental resources. The urgent need for new environmentally friendly solutions have made researchers explore new alternative materials that will reduce energy consumption, and greenhouse gas emissions (Hoy, Horpibulsuk, Rachan, Chinkulkijniwat, & Arulrajah, 2016). Highway pavement generally consists of base, subbase, and engineering fill layers, which are typically constructed from suitable materials such as crushed rock and lateritic soil. The government of Thailand's current priority is in the economic expansion of the country over the next decade and has allocated a large budget for the construction of roadway networks across the country. A number of road infrastructure projects have been implemented to construct transportation systems, particularly in rural areas. Heavy rain during the rainy season frequently causes flooding problems in some regions of Thailand. Hence, road embankments in the country must have an adequate thickness and must also be constructed with durable pavement materials. In general, the subbase/base layer is typically 50–70 cm in thickness, to ensure the road profile is above the flood level. Road construction consumes a vast amount of high-quality materials. The transportation of high-quality imported materials from distant sources increases the road construction cost considerably. Furthermore, transportation of imported materials significantly increases road maintenance costs and the carbon footprint. The utilization of local resources at the road construction site is thus beneficial from both economic and environmental aspects, which is an approach that is strongly encouraged by the Department of Rural Roads and the Department of Highways, Thailand (Sukprasert et al., 2021). The scientific and practical methodologies and outcomes from previous research have been reviewed and summarized in this paper in order to make a new illuminating study on cleaner production as well as to assure that waste materials can be mixed with soil as an intuitive practitioner interface technique in pavement applications (Sudla et al., 2018). For each road construction materials BA was used in highway embankment construction offers an attractive alternative to disposal because substantial economic savings can be attained by the reduction of ash disposal costs and the conservation of natural soils and lands, pavement construction (Gautam, Kalla,

Jethoo, Agrawal, & Singh, 2018; López-López, Vega-Zamanillo, Calzada-Pérez, & Taborga-Sedano, 2015; Yoo, Park, & Vo, 2016) and aggregate replacement in concrete pavement production (Arenas, Marrero, Leiva, Solís-Guzmán, & Arenas, 2011; Hannan et al., 2020; Ibrahim, Hamzah, Jamaluddin, Ramadhansyah, & Fadzil, 2015).

Within the context of sustainable material innovation, the integration of NRL modified bottom ash in geopolymer stabilization of RCA opens new avenues for high-performance base materials. The inclusion of NRL in the bottom ash geopolymer matrix introduces unique properties to the pavement base material. NRL, known for its elasticity and water resistance, imparts flexibility and resilience to the geopolymer-stabilized RCA. This modification is particularly beneficial for pavement applications, where materials are subjected to dynamic loads and environmental stresses. The NRL not only helps to absorb and distribute these loads more effectively, reducing the risk of cracking, but also provides a barrier against moisture infiltration, enhancing the durability of the pavement base.

Geopolymer is formed through the reaction of an aluminosilicate source, such as bottom ash (precursor), with an alkaline activator solution containing sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3). The alkaline activator solutions were prepared with various Na_2SiO_3 :NaOH (G/N) ratios of 1:1, 1:1.5, and 1:2, while the mixtures were modified with NRL at contents of 0.1, 0.2, and 0.3 by weight of the aggregate. The unconfined compressive strength (UCS) test was carried out to determine the strength of the studied mixtures at 7 and 28 days of curing. The strength development was examined through the microstructural and mineralogical analyses using scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD), respectively.

4.2 Materials and methods

4.2.1 Recycle Concrete Aggregate (RCA)

Recycled concrete aggregate (RCA) and bottom ash (BA) were used as waste materials in this research. RCA was collected from construction projects in Ubonratchatani and Sisaket Provinces, Thailand. The RCA had low moisture content (less than 0.3 wt%). Particle size distribution of air-dried RCA was determined by sieve analysis per ASTM-D422-63 (Testing & Materials, 2002). Figure 4.1 shows that the grading curve of RCA met specifications for pavement base material designated by the Department of Highways (DOH), Thailand. RCA had 48.6% gravel, 47.9% sand, and 3.5% fines (passing No. 200 sieve) and no plasticity. Based on the unified soil classification system (USCS) (ASTM-D2487-17, 2017), RCA was classified as well-graded gravel (GW).

The specific gravity of RCA was found to be 2.7. RCA had Los Angeles abrasion and flakiness index values of 38.1 and 15.6, respectively. The maximum dry unit weight was 18.70 kN/m^3 at an optimum moisture content of 12% based on a modified Proctor compaction test. Coarse and fine RCA water absorption was 6.42% and 7.83%, respectively.

The gradation of RCA was investigated by dry sieve analysis ASTM D422- 63. The grain size distribution curve of RCA complied with the grading limits for subgrade material Type D as shown in Figure 4.1 From the sieve analysis (% that passes through No. 200 sieve) and consistency limits (no plasticity), the RCA was classified as GP-SW according to the Unified Soil Classification System ASTM D2487. This is the group of poorly graded gravel to well-graded sand.

4.2.2 Bottom ash (BA)

Lignite bottom ash (BA) was sourced from the Mae Moh mine, the largest lignite power plant in northern Thailand, operated by the Electricity Generating Authority of Thailand (EGAT). BA particles were irregularly shaped with agglomerations, pores, and angular, rough surfaces, as observed by scanning electron microscopy (SEM) analysis Figure 4.1 and Table 3.1 summarizes the chemical composition of BA detected by X-ray fluorescent (XRF) analysis. The predominant component in the BA comprises the highest percentage of silicon dioxide (59.50%), which is a key ingredient that contributes to the pozzolanic activity of the ash. Followed by aluminum oxide (25.7%), which plays a crucial role in the geopolymerization process, reacting with the silicon dioxide and alkaline activator to form the geopolymer matrix. Constituting a low percentage (2.92%) of the ash, calcium oxide is known to affect the setting time and strength development in geopolymer.

Table 4.1 Chemical compositions of bottom ash.

Component (%)	Value
Silicon dioxide (SiO_2)	59.50
Aluminum oxide (Al_2O_3)	25.70
Iron oxide (Fe_2O_3)	6.07
Calcium oxide (CaO)	2.92
Magnesium oxide (MgO)	0.80
Potassium oxide (K_2O)	1.56

Lignite bottom ash came from the Mae Moh power station in the north of Thailand, This is the largest lignite power plant and is operated by the Electricity Generating Authority of Thailand (EGAT) used in this research, fresh bottom ash as shown in Figure 4.2 The as-received BA particles were relatively large and very irregular showing agglomeration of some spherical particles and other fragments with observable pores as shown in Figure 4.3(a). The particle shape and the size distribution were examined by scanning electron microscopy (SEM), and the chemical composition was determined by energy dispersive spectroscopy (EDS), and shown in Figure 4.3(b) respectively. The SEM images revealed that the particles were irregular with agglomeration of spherical particles and some angular and rough particles. The size distribution was similar to that of sand

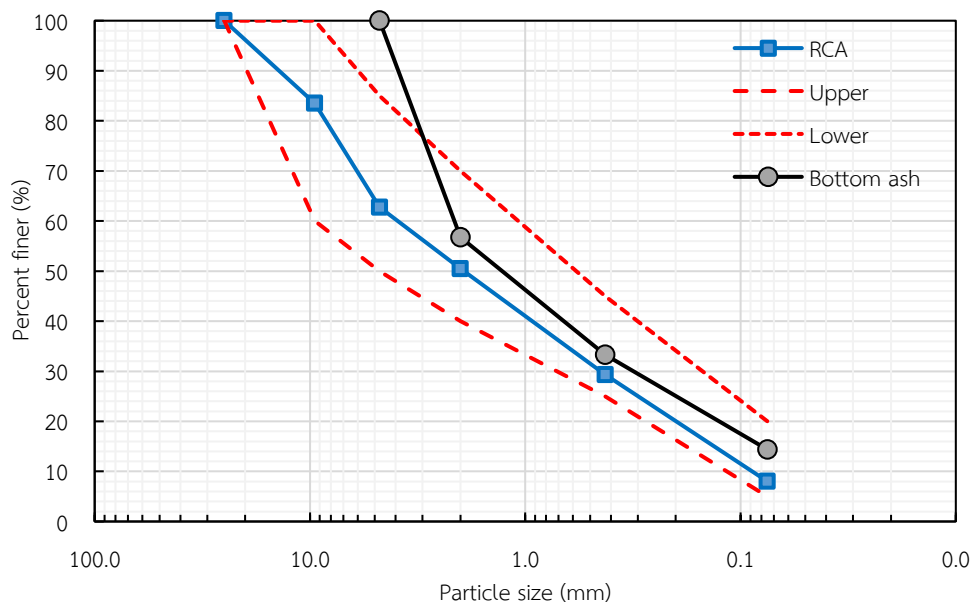


Figure 4.1 Grain size distribution of RCA and Bottom ash.

The gradation of BA was investigated by dry sieve analysis (ASTM D422- 63) (ASTM, 2007). The grain size distribution curve of BA complied with the grading limits for subgrade material Type D as per DH-S 205–1989 as shown in Figure 4.1 From the sieve analysis (% that passes through No. 200 sieve) and consistency limits (no plasticity), the BA was classified as SW-SM according to the Unified Soil Classification System (ASTM D2487) (ASTM, 2007). This is the group of well-graded sand with silty fines.

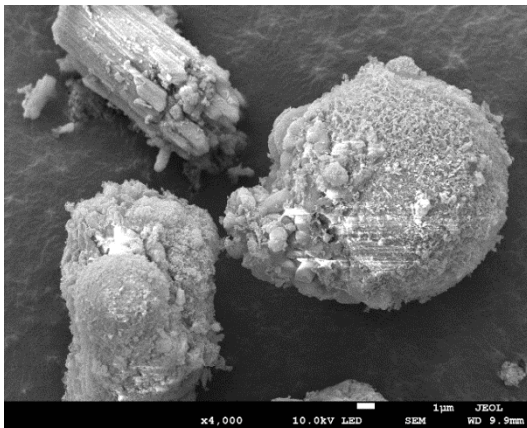


(a) Mea Moh power plant Thailand

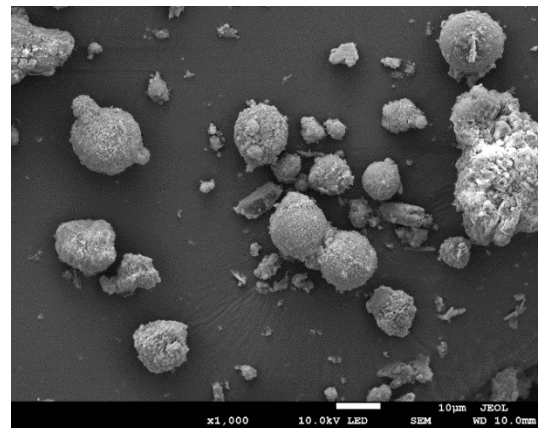


(b) Ground bottom ash

Figure 4.2 Fresh Bottom ash at Mea Moh power plant, Thailand.



(a) As-received bottom ash



(b) ground bottom ash

Figure 4.3 SEM of as-received bottom ash and ground bottom ash (a) As-received bottom ash and (b) ground bottom ash.

Figure 4.4 illustrates the X-ray diffraction (XRD) pattern of BA. The peak intensities, denoted by their counts, show the relative abundance of the minerals, with gehlenite and diopside being the most prominent. The diversity of crystalline phases indicates that the BA can provide a key role when used as a precursor in geopolymer production, contributing to the mechanical properties.

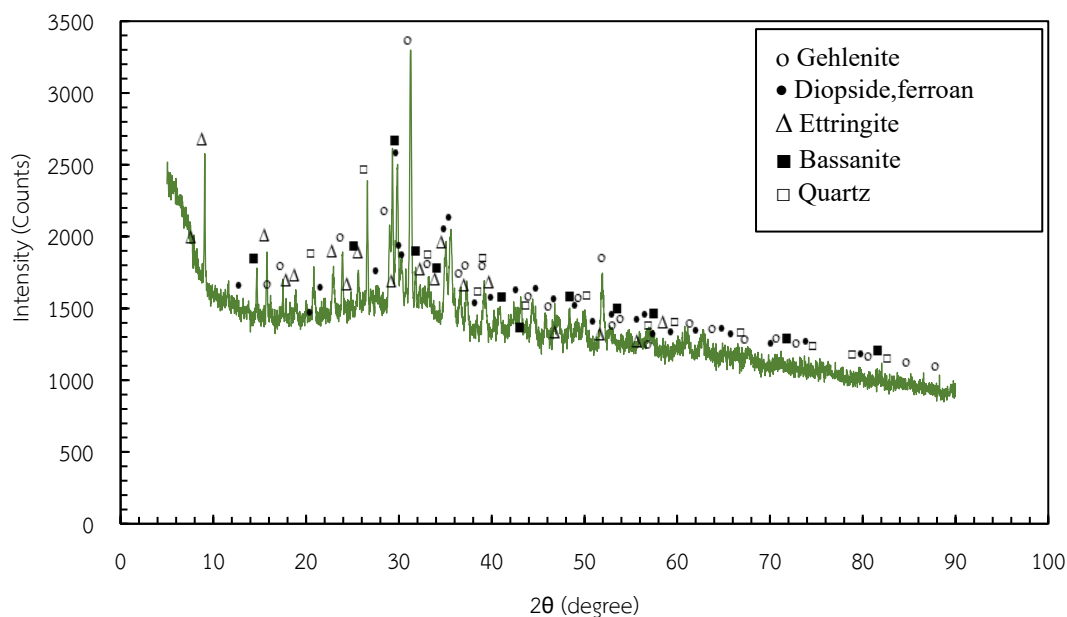


Figure 4.4 XRD pattern of bottom ash.

4.2.3 Natural rubber latex (NRL)

The natural rubber latex (NRL) used in this study was of a low ammonia concentrated latex type, conforming to the ISO 2004-1988 standard. The NRL was used as an additive to enhance the properties of BA-based geopolymer stabilized RCA. NRL was treated with deproteinization agent to remove allergenic proteins, improve latex stability, enhance compatibility with other components, and ultimately contribute to better mechanical properties in the final product. The NRL in this study was in a liquid form, containing both solid and liquid constituents. The total solid content of NRL accounted for 33.06% of its weight, comprising primarily of dry rubber (30.8%), sludge (2.46%), and a minimal coagulum content (0.024%). The specific gravity and pH of the NRL were 0.96 and 8, respectively.

4.2.4 Alkaline activator

The formulation of the alkaline activator was a critical step in the geopolymer preparation process. It required careful consideration of the chemical composition to ensure effective geopolymerization while minimizing potential hazards. In this study, an alkaline activator was formulated by blending sodium silicate (Na_2SiO_3) solution with 5M sodium hydroxide (NaOH) solution. The selected Na_2SiO_3 was Type CR53, which contained about 14.5-16.5 wt% Na_2O (sodium oxide) and 31.5-34 wt% SiO_2 (silicon dioxide), providing an optimal balance of silica and sodium necessary for the

geopolymerization process. The selection of a 5M NaOH solution was particularly informed by considerations regarding human safety and handling hazards. Previous study (Chindaprasirt, Jaturapitakkul, Chalee, & Rattanasak, 2009) have indicated that higher concentrations of NaOH can pose increased risks due to its highly caustic nature. Hence, the 5M concentration was deemed effective in initiating the dissolution of aluminosilicate materials while maintaining a safer profile for practical use.

4.2.5 Mix design and sample preparation

The mix design for this study was systematically developed to evaluate the impact of NRL modification on the properties of BA-based geopolymer stabilized RCA (Table 2). The design involved creating a series of mixtures with varying NRL content and alkaline activator ratios to establish a comprehensive understanding of their individual and combined effects on the geopolymer's performance.

The control mix, designated as RCA70BA30, consisted of 70% RCA and 30% BA by weight, mixed solely with water without any alkaline activator or NRL. This baseline mixture was intended to assess the fundamental properties of the RCA-BA blend.

A series of NRL-modified mixtures were prepared with a constant $\text{Na}_2\text{SiO}_3/\text{NaOH}$ (G/N) ratio of 1, while the NRL content was varied at 0.1%, 0.2%, and 0.3% by weight of aggregate (sample IDs: GN1/1NRL0.1, GN1/1NRL0.2, and GN1/1NRL0.3). Additional mixtures were designed with increased $\text{Na}_2\text{SiO}_3/\text{NaOH}$ (G/N) ratios of 1.5 to 2, with corresponding NRL contents of 0.1%, 0.2%, and 0.3%, respectively (Sample IDs: GN1/1.5NRL0.1, GN1/1.5NRL0.2, GN1/1.5NRL0.3, and GN1/2NRL0.1, GN1/2NRL0.2, GN1/2NRL0.3).

The RCA and BA were first dry-mixed to achieve a uniform distribution. The alkaline activator solution was then gradually added to the dry mixture and mixed until a homogenous mixture was obtained. Then, NRL was added to the mixture in the predetermined percentage, ensuring thorough blending for even distribution within the mixture. The resulting mixtures were cast into the cylindrical mold with 101.6 mm in diameter and 116.4 mm in height. Each mixture was compacted under a modified Proctor compaction effort to determine its maximum dry density (MDD) and optimum liquid content (OLC). The sample was then prepared at MDD and OLC of each studied mixture for unconfined compressive strength test. Samples were covered with plastic sheeting to prevent moisture loss and cured at room temperature for 24 hours before demolding. After demolding, the samples were further cured at room temperature ($25\pm 2^\circ$) until the testing ages at 7 and 28 days.

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Table 4.2 The mix design of NRL-modified BA-based geopolymer stabilized RCA

Sample ID	Mixture ingredient	Alkaline Activator	NRL (%)
		NaOH/Na ₂ SiO ₃ (G/N) ratio	By weight of aggregate
70RCA30BA	70RCA + 30BA + water (Control)	-	-
G/N1:1NRL0.1	70RCA + 30BA + (1) NaOH + (1) Na ₂ SiO ₃ + NRL (0.1)	1	0.1
G/N1:1NRL0.2	70RCA + 30BA + (1) NaOH + (1) Na ₂ SiO ₃ + NRL (0.2)	1	0.2
G/N1:1NRL0.3	70RCA + 30BA + (1) NaOH + (1) Na ₂ SiO ₃ + NRL (0.3)	1	0.3
G/N1:1.5NRL0.1	70RCA + 30BA + (1) NaOH + (1.5) Na ₂ SiO ₃ + NRL (0.1)	1.5	0.1
G/N1:1.5NRL0.2	70RCA + 30BA + (1) NaOH + (1.5) Na ₂ SiO ₃ + NRL (0.2)	1.5	0.2
G/N1:1.5NRL0.3	70RCA + 30BA + (1) NaOH + (1.5) Na ₂ SiO ₃ + NRL (0.3)	1.5	0.3
G/N1:2NRL0.1	70RCA + 30BA + (1) NaOH + (2) Na ₂ SiO ₃ + NRL (0.1)	2	0.1
G/N1:2NRL0.2	70RCA + 30BA + (1) NaOH + (2) Na ₂ SiO ₃ + NRL (0.2)	2	0.2
G/N1:2NRL0.3	70RCA + 30BA + (1) NaOH + (2) Na ₂ SiO ₃ + NRL (0.3)	2	0.3

The control mix, designated as RCA70BA30, consisted of 70% RCA and 30% BA by weight, mixed solely with water without any alkaline activator or NRL. This baseline mixture was intended to assess the fundamental properties of the RCA-BA blend.

A series of NRL-modified mixtures were prepared with a constant $\text{Na}_2\text{SiO}_3/\text{NaOH}$ (G/N) ratio of 1, while the NRL content was varied at 0.1%, 0.2%, and 0.3% by weight of aggregate (sample IDs: GN1/1NRL0.1, GN1/1NRL0.2, and GN1/1NRL0.3). Additional mixtures were designed with increased $\text{Na}_2\text{SiO}_3/\text{NaOH}$ (G/N) ratios of 1.5 to 2, with corresponding NRL contents of 0.1%, 0.2%, and 0.3%, respectively (Sample IDs: GN1/1.5NRL0.1, GN1/1.5NRL0.2, GN1/1.5NRL0.3, and GN1/2NRL0.1, GN1/2NRL0.2, GN1/2NRL0.3).

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4.3.1 Laboratory Experimental Program

The experimental program was meticulously designed to evaluate the mechanical and microstructural properties of NRL-modified BA-based geopolymers stabilized RCA. The program consisted of two main testing categories: mechanical tests and microstructural analysis.

4.3.2 Modified compaction test

Samples were prepared in accordance with the modified Proctor compaction test according to the ASTM D1557 (ASTM, 2012) (ASTM-D1557-12, 2012; ASTM, 2012), ensuring optimal compaction and consistent density across all samples. The compaction procedure was instrumental in simulating field compaction conditions and providing samples that represent the maximum dry density (MDD) and optimal liquid content (OLC).

4.3.3 Unconfined compressive strength

Following curing at 7 and 28 days, the samples were subjected to an unconfined compressive strength (UCS) test. The UCS test was conducted in compliance with ASTM D2166 (ASTM-D2166-06, 2006), providing a measure of the material's strength when subjected to axial loading conditions. The test was performed

at a rate of 1mm/min to track the strength development of the geopolymer over time. The peak load at failure was recorded, and the compressive strength was calculated to assess the NRL's contribution to the overall structural integrity of the geopolymer matrix.

4.3.4 Scanning Electron Microscopy (SEM) analysis

Scanning electron microscopy (SEM) analysis was employed to visualize the microstructure of the geopolymer samples at a high magnification. This analysis provides insights into the distribution of NRL within the matrix, the bonding at the RCA-BA interface, and the morphology of the geopolymer binder. The SEM examination was conducted on fractured samples post-UCS testing to identify the failure mechanisms and to correlate the mechanical test results with the microstructural characteristics.

4.3.5 X-Ray Diffraction (XRD) analysis

X-ray diffraction (XRD) analysis was utilized to identify the crystalline phases present within the geopolymer matrix and to observe the changes in mineralogy due to the addition of NRL and variation in the alkaline activator mixture. The XRD patterns were collected using a diffractometer, with samples being scanned in a 2Theta range typically between 5° and 80°. The resultant diffractograms were analyzed to determine the presence of specific crystalline compounds and to infer the geopolymerization process's effectiveness.

4.4 Results and Discussion

4.4.1 Unconfined compressive strength development

The unconfined compressive strength (UCS) results, as shown in Figure 4.5, demonstrate the influence of NRL content and alkaline activator ratio on the strength development of BA-based geopolymer stabilized RCA mixtures at 7 and 28 days of curing.

At 7 days, the UCS values of the NRL-modified mixtures ranged from 1.30 to 4.05 MPa, while the control mix (RCA70BA30 blend) exhibited a UCS of 0.63 MPa. The highest UCS was achieved by the mixture with 0.1% NRL and a G/N ratio of 1:1, followed by the mixtures with 0.2% and 0.3% NRL at the same G/N ratio. This trend suggests that a lower NRL content and a balanced G/N ratio contribute to better early-age strength development.

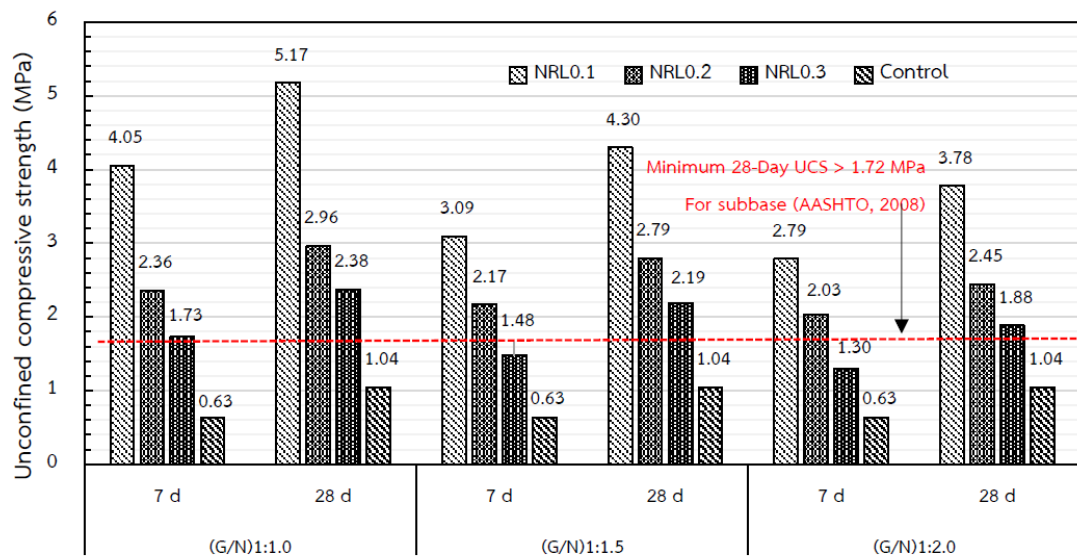


Figure 4.5 UCS of NRL-modified BA-based geopolymer stabilized RCA samples.

After 28 days of curing, the UCS values of the NRL-modified mixtures increased significantly, ranging from 1.88 to 5.17 MPa, while the control mix reached 1.04 MPa. The mixture with 0.1% NRL and a G/N ratio of 1:1 continued to exhibit the highest UCS, indicating its optimal composition for strength development. The mixtures with higher G/N ratios (1:1.5 and 1:2) showed relatively lower UCS values compared to those with a G/N ratio of 1:1. This implies that an excessive amount of sodium silicate in the alkaline activator may hinder the strength gain. This may be due to the optimal silica to alumina ratio, which is critical in forming a strong geopolymer network. However, as the silica content increased in the activator solution (G/N ratio of 1:1.5 and 1:2), the UCS values tended to decrease. This decrease could be attributed to an excess of silica leading to a less reactive system where the silica is not effectively utilized, resulting in a weaker matrix.

The American Association of State Highway and Transportation Officials (AASHTO) provides guidance on the minimum strength requirements for pavement layers in their mechanics-empirical pavement design guide (MEPDG), which indicates that the minimum 28-day UCS requirement for a subbase material is 1.72 MPa (AASHTO, 2008). This strength criterion ensures that the subbase layer possesses sufficient bearing capacity and stability to support the upper pavement layers and distribute the traffic loads effectively to underlying layers.

Figure 4.5 evident that all the NRL-modified BA-based geopolymer stabilized RCA mixtures, irrespective of the G/N ratio (1:1, 1:1/5, and 1:2) or NRL content (0.1%, 0.2, and 0.3%), surpass the minimum requirement of 1.72 MPa specified by AASHTO (2008) for subbase materials. It is noteworthy that even the control mixture (RCA70BA30 blend without geopolymer or NRL modification) achieves a 28-day UCS of 1.0 MPa, which is lower than the minimum requirement of 1.72 MPa for subbase materials. This indicates the significant enhancement in strength and performance brought about by the NRL-modified BA-based geopolymer stabilization of the RCA.

The synergistic effect of the alkaline activator ratio (G/N) and NRL content on the strength development of BA-based geopolymer stabilized RCA mixture is evident from the UCS results. The combination of a lower G/N ratio and an optimal NRL content leads to a remarkable improvement in the mechanical properties of the stabilized mixtures. The lower G/N ratio of 1:1 ensures a sufficient concentration of sodium hydroxide, which is essential for the dissolution of the aluminosilicate precursors and the formation of a stable geopolymer gel. Simultaneously, the presence of NRL at an optimum content of 0.1% or 0.2% improves the adhesion between the RCA particles and the geopolymer matrix, resulting in a more compact and resilient structure. This synergistic effect is particularly evident when comparing the UCS values of the mixtures with different G/N ratios and NRL contents. The mixture with 0.1% NRL at a G/N ratio of 1:1 achieved the highest UCS of 4.05 MPa at 7 days and 5.17 MPa at 28 days, surpassing the minimum requirements for both low-volume and high-volume traffic pavements. In contrast, mixtures with higher G/N ratios or excessive NRL contents showed relatively lower UCS values, indicating the importance of optimizing both parameters simultaneously.

The synergy between the G/N ratio and NRL content not only enhances the strength development but also contributes to the overall performance and durability of the stabilized mixtures. The optimized combination of these two factors results in a geopolymer matrix with improved bonding, flexibility, and resistance to cracking, which are crucial for the long-term performance of pavement base materials.

These results highlight the effectiveness of NRL modification in enhancing the strength properties of BA-based geopolymer stabilized RCA mixtures. The incorporation of NRL improves the bonding between the RCA and the geopolymer matrix, leading to better load transfer and high compressive strength. The optimal NRL content and G/N ratio identified in this study, particularly the mixture with 0.1% NRL at a G/N ratio of 1:1, demonstrate the potential for developing high-performance and

sustainable pavement base materials that can meet the strength requirements for both low-volume and high-volume traffic pavements.

4.4.2 Microstructural Analysis

The scanning electron microscopy (SEM) analysis provides valuable insights into the microstructural characteristics of the NRL-modified BA-based geopolymer stabilized RCA mixtures. The SEM images illustrate the influence of the G/N ratio and NRL content on the morphology, bonding, and formation of geopolymer products within the matrix.

4.4.3 Effect of G/N ratio on microstructural property

The effect of the G/N ratio on the microstructure is illustrated in Figure 4.6, which presents the SEM images of the control mixture (RCA70BA30) and NRL-modified BA-based geopolymer mixtures with varying G/N ratios (1:1, 1:1.5, and 1:2) at a constant NRL content of 0.1%. The control mixture (Figure 4.6a) exhibits a relatively porous and heterogeneous microstructure, with visible voids and weak bonding between the RCA and BA particles, which corresponds with its lower UCS values as shown in Figure 4.5. In contrast, the NRL-modified BA-based geopolymer mixture with a G/N ratio of 1:1 (Figure 4.6b) shows a more compact and denser microstructure, with enhanced bonding between the RCA particles and the matrix. This improvement in microstructural properties can be attributed to the balanced composition of the alkaline activator (G/N), which facilitates effective geopolymerization and the formation of stable geopolymer products, such as calcium aluminosilicate hydrate (C-A-S-H) and sodium aluminosilicate hydrate (N-A-S-H) gels (Provis & Van Deventer, 2009; Yip, Lukey, Provis, & Van Deventer, 2008). (Santa, Padoin, Soares, and Riella (2021) indicated that the geopolymerization of the BA-based geopolymer involves the dissolution of the aluminosilicate material such as BA in an alkaline activator solution, followed by the polycondensation of the leached Al and Si species to form the geopolymer gels. The presence of these gels is critical for the strength development and durability of the geopolymer matrix (Davidovits, 2005; Peter Duxson et al., 2007; Duxson, Mallicoat, Lukey, Kriven, & Van Deventer, 2007). The NRL films can be observed as thin, bridging structures that enhance the interfacial bonding between the RCA particles and the geopolymer gel products.

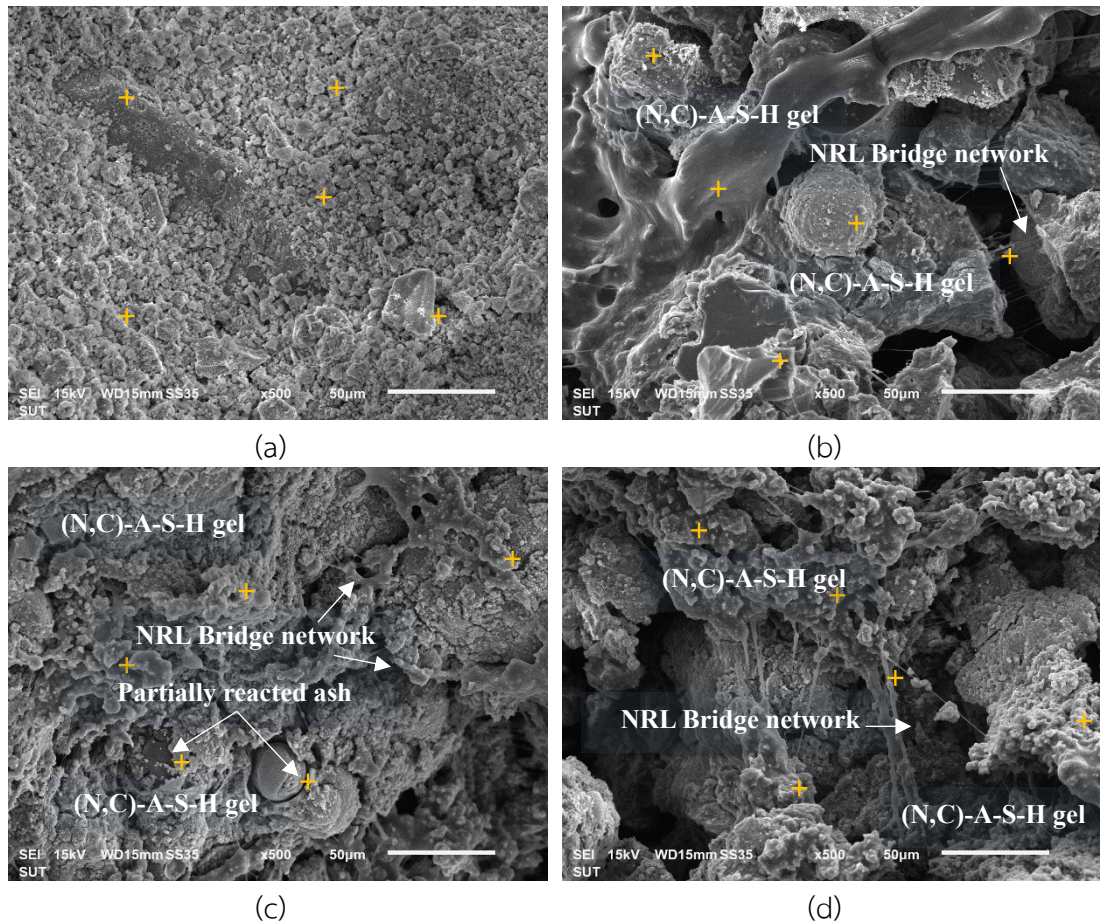


Figure 4.6 SEM-EDX analysis of NRL-modified BA-based geopolymer stabilized RCA samples: a) RCA70BA30 (Control), b) G/N1:1.0NRL0.1, c) G/N1:1.5NRL0.1, and d) G/N1:2.0NRL0.1.

As the G/N ratio increases to 1:1.5 (Figure 4.6c) and 1:2 (Figure 4.6d), the NRL films are still present, acting as bridging structures, but the overall microstructure is notably change compared to the mixture with a G/N ratio of 1:1. It is found that an overly high silica content can lead to the formation of a silica-rich gel layer on the surface of the BA and RCA particles, hindering the further dissolution of aluminosilicate species and resulting in an incomplete geopolymerization reaction. In other word, the excess soluble silica provided by the sodium silicate (Na_2SiO_3) contributes to the formation of a more silica-rich gel, known as poly(sialate-siloxo) or PSS gel (Bhagath Singh & Subramaniam, 2017; Kim, Dang, & Do, 2016; M, R, & P, 2021). It can form a barrier layer on the surface of the unreacted particle, lead to weaken the overall strength and integrity of the geopolymer matrix.

The EDX analysis presented in Table 4.3 provides insights into the elemental composition of the NRL-modified BA-based geopolymer stabilized RCA mixtures. The major elements analyzed include carbon (C), oxygen (O), iron (Fe), sodium (Na), calcium (Ca), aluminum (Al), and silicon (Si). Several research reported that Si/Al ratio is a crucial parameter influencing the geopolymerization process and the properties of the resulting geopolymer (Davidovits, 2005; Peter Duxson et al., 2007; PSWM Duxson et al., 2007). The control mixture, consisting of 70%RCA and 30%BA without any geopolymer or NRL, serves as a baseline for comparison. The EDX analysis reveals that the control mixture has a high Si/Al ratio of 17.6, indicating a predominance of silicon-rich compounds in the blend. The presence of calcium (1.83%) suggests the potential formation of calcium-containing phases, such as calcium silicate hydrate (C-S-H) in the mixture.

Table 4.3 EDX analysis of NRL-modified BA-based geopolymer stabilized RCA mixtures.

Sample IDs	Major elements analyzed (all results in weight%)							Si/Al ratio
	C	O	Fe	Na	Ca	Al	Si	
70RCA30BA (control)	9.57	51.82	1.07	4.87	1.83	1.75	30.74	17.6
G/N1:1.0NRL0.1	37.90	31.15	1.05	2.54	6.69	3.03	17.62	5.80
G/N1:1.5NRL0.1	39.28	32.67	1.33	2.63	6.75	2.38	16.79	7.10
G/N1:2.0NRL0.1	38.94	33.34	1.45	2.79	6.81	1.88	15.72	8.40

The incorporation of the NRL and BA-based geopolymer in the RCA mixture leads to significant changes in the elemental composition of G/N1:1NRL0.1 mixture compared to the control mixture. The Si/Al ratio decreases from 17.6 in the control mixtures to 5.80 in the G/N1:1NRL0.1 mixture. This decrease can be attributed to the dissolution of aluminum-rich compounds from the BA during the geopolymer process, resulting in a lower Si/Al in the geopolymer gel. In addition, the G/N1:1NRL0.1 mixture exhibits a higher calcium content (6.69%) compared to the control mixture. The increase in calcium content can be attributed to the formation of calcium aluminosilicate hydrate (C-A-S-H) gel alongside the sodium aluminosilicate hydrate (N-A-S-H) gel in the geopolymer matrix.

As the G/N ratio increases from 1:1 to 1:1.5, and 1:2, the Si/Al ratio in the stabilized mixtures also increases from 5.80 to 7.10 and 8.40, respectively. This

increase in the Si/Al ratio can be attributed to the higher amount of soluble silica provided by the increased Na_2SiO_3 content in the alkaline activator solution.

The optimized combination of NRL content and G/N ratio in the NRL-modified mixtures, particularly the mixture with 0.1% NRL and a G/N ratio of 1:1, capitalizes on the beneficial effects of a lower Si/Al ratio and the presence of calcium. This synergistic effect contributes to the enhanced mechanical properties and microstructural characteristics of the NRL-modified BA-based geopolymer stabilized RCA mixtures.

4.4.4 Effect of NRL on microstructural property

Figure 4.7 presents the SEM images of NRL-modified mixtures with varying NRL contents (0.1%, 0.2%, and 0.3%) at a constant G/N ratio of 1:1. The mixture with 0.1% NRL (Figure 4.7a) exhibits a dense and homogeneous microstructure, with a well-developed geopolymer gel network. The NRL films form thin, continuous bridging structures that enhance the interface bonding between the RCA particles and geopolymer matrix.

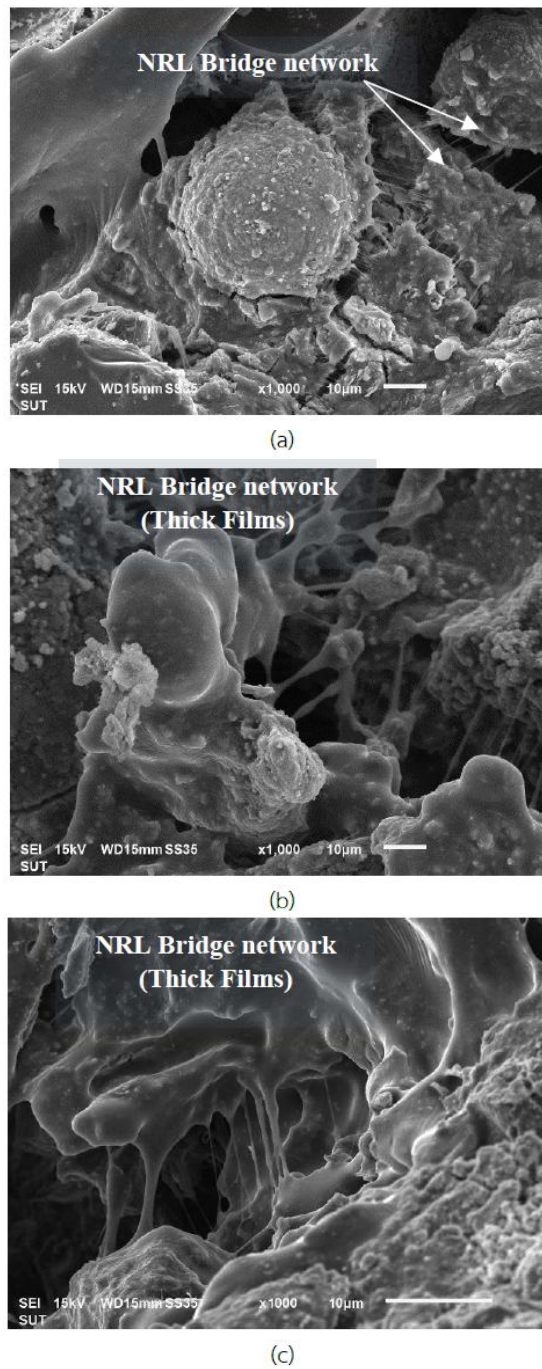


Figure 4.7 SEM images of NRL-modified BA-based geopolymer stabilized RCA samples: a) G/N1:1.0NRL0.1, b) G/N1:1.0NRL0.2, and c) G/N1:1.0NRL0.3

The physical interaction is related to the mechanical interlocking of the NRL film with the rough and porous surface of the matrix. The NRL film penetrates into the surface irregularities and pores of the RCA particles, creating a physical anchor that enhances the bond strength between the particles and the matrix. This implies that

the synergistic characteristic between the NRL films and geopolymer gels can lead to enhance the strength development of BA-based geopolymer stabilized RCA.

As the NRL content increases to 0.2% (Figure 4.7b) and 0.3% (Figure 4.7c), the microstructure remains relatively compact and homogeneous, but the NRL films become thicker and more prominent. The thicker NRL films may contribute to a slightly more ductile behavior of the geopolymer matrix. However, the excessive thickness of the NRL films at higher content may lead to a decrease in dissolution of aluminosilicate-rich BA during the geopolymer process and resulted in sluggish strength development. The findings indicate an intricate interplay between the G/N ratio, NRL content, and the resulting UCS. The microstructural observations from the SEM-EDX analysis corroborate the findings from the UCS results, where the mixture with 0.1% NRL and a G/N ratio of 1:1 exhibited the highest strength development. The dense and homogeneous microstructure, the presence of well-developed (N,C)-A-S-H gels, and the effective bridging mechanism provided by the thin NRL films contribute to the superior mechanical performance of this mixture.

4.4.5 XRD analysis

The XRD analysis provides valuable information on the mineralogical composition and the formation of geopolymer reaction products in the NRL-modified BA-based geopolymer stabilized RCA mixtures. To investigate the influence of NRL content and G/N ratios on the polymerization process and the resulting geopolymer products, the XRD patterns of NRL-modified samples with varying G/N ratios and NRL contents were examined and compared with the control sample (RCA70BA30).

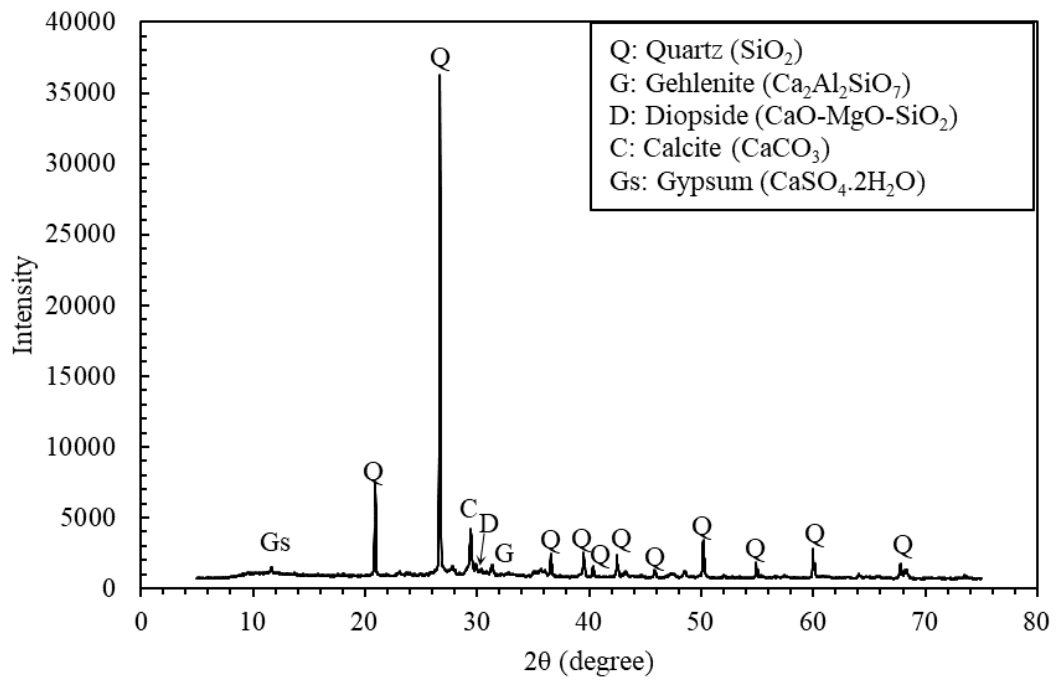


Figure 4.8 XRD patterns of RCA70BA30 (Control sample).

Figure 4.8 illustrates the XRD patterns of the control sample, which consists of 70%RCA and 30% BA without any geopolymer or NRL modification. The XRD pattern exhibits sharp peaks corresponding to the crystalline phases present in the RCA and BA, such as quartz (SiO_2), calcite (CaCO_3), and hematite (Fe_2O_3). The absence of broad humps in the XRD pattern indicates the lack of amorphous geopolymer gel formation in the control sample.

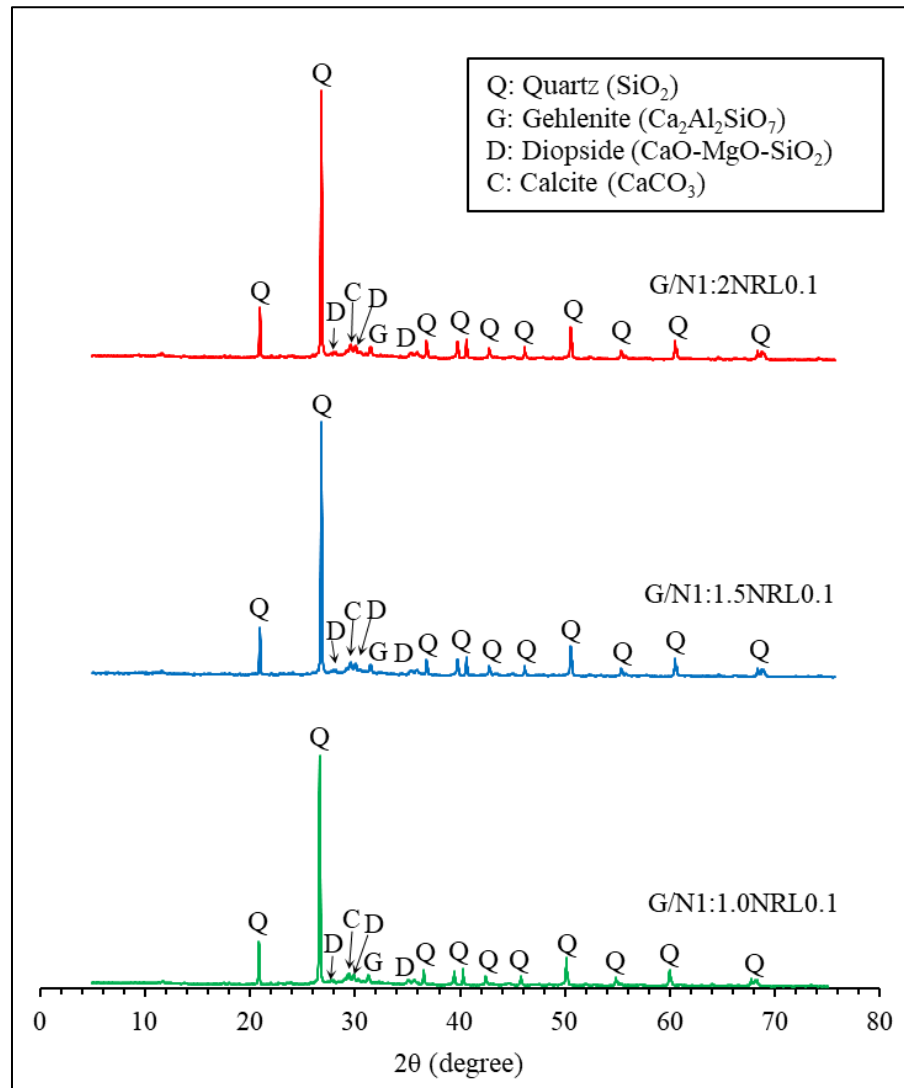


Figure 4.9 XRD patterns of NRL-modified BA-based geopolymer stabilized RCA samples.

Figure 4.9 demonstrates the XRD patterns of the NRL-modified BA-based geopolymer stabilized RCA samples with varying G/N ratios (1:1, 1:1.5, and 1:2) at a constant NRL content of 0.1%. The XRD patterns of the NRL-modified samples exhibit a notable reduction in the intensity of the crystalline peaks compared to the control sample. This reduction in peak intensity suggests the dissolution of the crystalline phases and the formation of amorphous geopolymer gel products (El Alouani et al., 2024; Sinha, Kumar, & Kumar, 2014). In addition, the XRD patterns show a gradual increase in the background hump between 20° and 40° 2θ , indicating the formation of amorphous geopolymer gel (Bobirić et al., 2020). The broad hump is more pronounced in the sample with a G/N ratio of 1:1, implying a higher degree of geopolymerization and the formation of a more extensive amorphous geopolymer network.

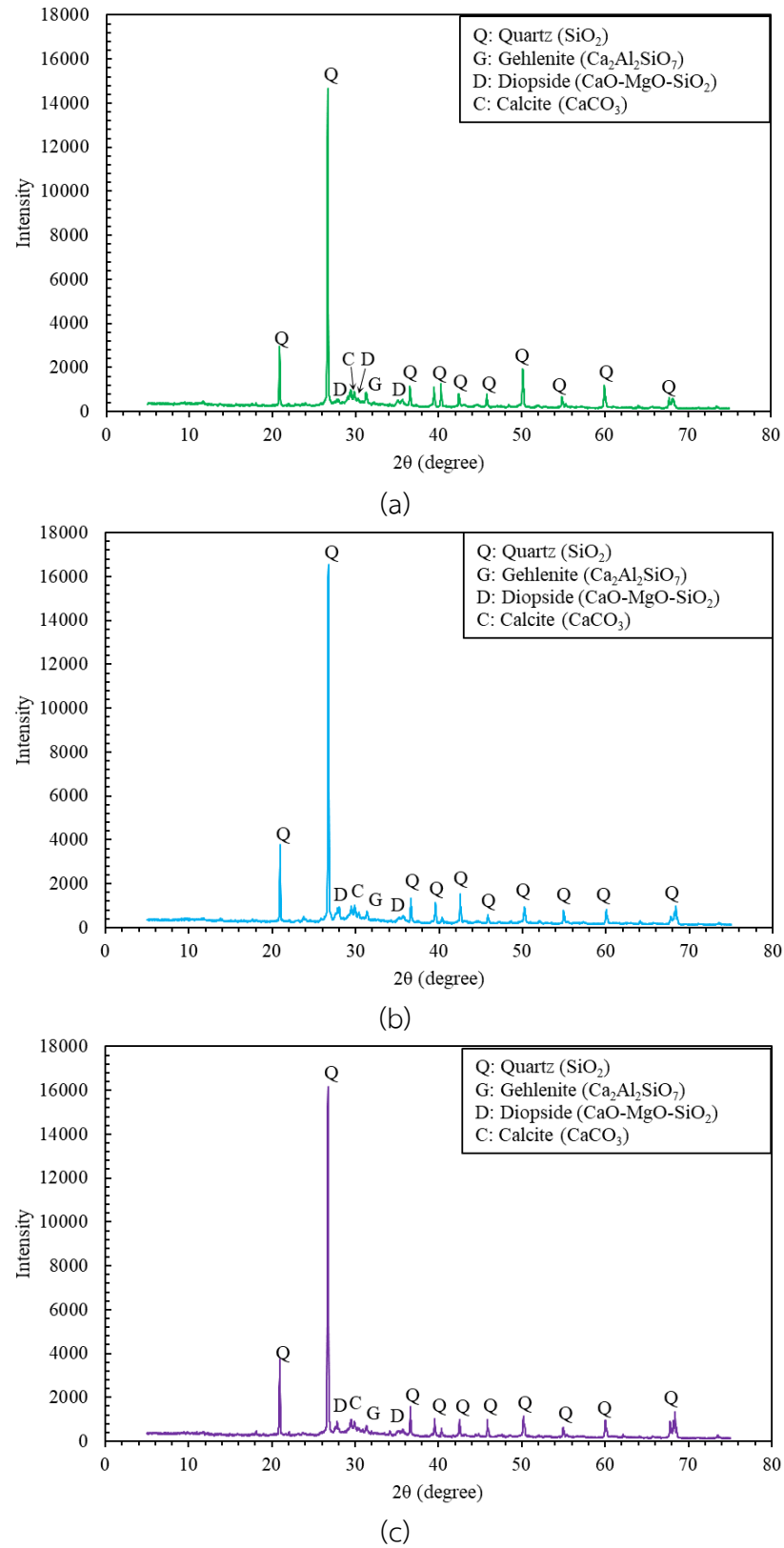


Figure 4.10 XRD patterns of NRL-modified BA-based geopolymer stabilized RCA samples:
a) G/N1:1.0NRL0.1, b) G/N1:1.0NRL0.2, c) G/N1:1.0NRL0.3

Figure 4.10 presents the XRD patterns of the NRL-modified BA-based geopolymer stabilized RCA samples with varying NRL contents (0.1%, 0.2%, and 0.3%) at a constant G/N ratio of 1:1. The XRD patterns of the NRL-modified samples show a significant reduction in the intensity of the crystalline peaks compared to the control sample, indicating the dissolution of the crystalline phases and the formation of amorphous geopolymer gel (Kumar & Revathi, 2020). The sample with 0.1% NRL shows the lowest intensity of the crystalline peaks and most pronounced broad hump, indicating the optimal NRL content for promoting geopolymerization and the formation of amorphous geopolymer gel products. Furthermore, as the NRL content increase from 0.1% to 0.3%, the XRD patterns reveal the presence of residual crystalline phases, such as quartz and calcite, which have not been completely dissolved during the geopolymerization process. As a result, a slow strength development was gain.

The XRD analysis supports the findings from the microstructural characterization by SEM analysis and the mechanical testing that G/N ratio and NRL content play a significant role in the geopolymerization process. It was found that the sample containing 0.1% NRL and a G/N ratio of 1:1 exhibiting the most pronounced geopolymerization and amorphous geopolymer gel formation. This finding highlights the effectiveness of the NRL-modified BA-based geopolymer in stabilizing RCA and producing a sustainable and high-performance pavement base material.

4.5 Conclusion

The present study investigated the performance of natural rubber latex (NRL) modified bottom ash (BA)-based geopolymer stabilized recycled concrete aggregate (RCA) as a sustainable pavement base material. The influence factors studies, including NRL content (0.1%, 0.2%, and 0.3% by weight of aggregate) and alkaline activator ratios ($\text{NaOH}:\text{Na}_2\text{SiO}_3$ (G/N) = 1:1, 1:1.5, and 1:2) on the strength development of the mixture. The main findings of the research are as follows:

- 1) The incorporation of NRL and the optimization of the alkaline activator ratio significantly enhanced the unconfined compressive strength (UCS) of the stabilized RCA mixtures. All the NRL-modified BA-based geopolymer stabilized RCA mixtures, irrespective of the G/N ratio (1:1, 1:1.5, and 1:2) or NRL content (0.1%, 0.2%, and 0.3%), surpass the minimum requirement of 1.72 MPa for subbase materials. The mixture containing 0.1% NRL and a G/N ratio of 1:1 achieved the highest UCS values of 4.05 MPa and 5.17 MPa at 7 and 28 days, respectively. However, the UCS values of all stabilized RCA mixture decreased with increasing G/N ratios and/or NRL ratios.

2) The microstructure analyses, including SEM, EDX, and XRD, revealed the formation of a dense and homogeneous geopolymer matrix in the NRL-modified mixtures. The NRL films acted as bridging structures that enhanced the bonding between RCA particles and the matrix, contributing to the improved mechanical properties.

3) The alkaline activator ratio and NRL content played a crucial role in the geopolymerization process and the strength development of the stabilized mixtures. The XRD analysis confirmed the dissolution of crystalline phase and the formation of amorphous geopolymer gel in the NRL-modified mixtures, with the mixture containing 0.1% NRL and a NaOH:Na₂SiO₃ ratio of 1:1 exhibiting the most pronounced geopolymerization.

4) A balanced NaOH:Na₂SiO₃ ratio of 1:1 promoted the formation of a stable geopolymer gel, while higher ratios led to a silica-rich gel that hindered further geopolymerization and strength gain. Meanwhile, excessive amounts of NRL led to a reduction in strength compared to the mixture with 0.1% NRL. This suggests that there is an optimal NRL content beyond which the strength development is hindered, possibly due to the formation of thicker NRL films that may interfere with the geopolymerization process.

The findings of this study demonstrate the potential of NRL-modified bottom ash-based geopolymer stabilized RCA as an eco-friendly and high-performance alternative to conventional pavement base materials, provided that the NRL content is optimized. The utilization of waste materials, such as RCA and bottom ash, coupled with the innovative use of NRL as a modifier, contributes to the development of sustainable pavement solutions.

4.6 Reference

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