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Review

Utilisation of Waste-Based Geopolymer in Asphalt Pavement Modification and Construction; A Review

Abdalrhman Milad [1,*], Ahmed Suliman B. Ali [2], Ali Mohammed Babalghaith [3], Zubair Ahmed Memon [4,*], Nuha S. Mashaan [5], Salaheddin Arafa [2] and Nur Izzi Md. Yusoff [1]

1 Department of Civil Engineering, Universiti Kebangsaan Malaysia, UKM Bangi 43600, Selangor, Malaysia; izzi@ukm.edu.my
2 Faculty of Civil Engineering and Built Environment, University Tun Hussein Onn Malaysia, Parit Raja 86400, Johor, Malaysia; algowel@yahoo.com (A.S.B.A.); arafa.uthm@gmail.com (S.A.)
3 Centre for Transportation Research, Department of Civil Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia; bablgeath@hotmail.com
4 Department of Engineering Management, College of Engineering, Prince Sultan University (PSU), Riyadh 11586, Saudi Arabia
5 School of Civil & Mechanical Engineering, Curtin University, Bentley, WA 6102, Australia; nuhas.mashaan1@curtin.edu.au
* Correspondence: miladabdalrhman@siswa.ukm.edu.my (A.M.); zamemon@psu.edu.sa (Z.A.M.)

Abstract: The use of geopolymer in pavement constructions is strongly encouraged. Many studies have demonstrated the vast potential of using industrial-by-products-based geopolymers. This paper discusses the modification of asphalt binders with geopolymers, namely geopolymer-modified asphalt (GMA) and geopolymer-modified asphalt mixture (GMAM). In addition, curing geopolymer materials, engineering properties, production techniques, and prospective utilisation in the pavement construction, such as durability and sustainability, are also discussed. The literature review showed that many industrial by-products, including red mud, blast furnace slag, fly ash, and mine waste, are used to produce geopolymers because of the metal components such as silicon and aluminium in these materials. The geopolymers from these materials influence the rheological and physical properties of asphalt binders. Geopolymers can enhance asphalt mixture performance, such as stability, fatigue, rutting, and low-temperature cracking. The use of geopolymers in asphalt pavement has beneficial impacts on sustainability and economic and environmental benefits.

Keywords: geopolymers; eco-friendly; asphalt pavement industry; hot-mix asphalt; warm-mix asphalt; reclaimed asphalt pavement; industrial wastes

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1. Introduction

Geopolymers are amorphous inorganic materials prepared by the activation of aluminosilicate precursors with hydroxides, carbonates, or silicates of alkali or alkaline earth metals [1]. These materials are considered greener materials because of their lower carbon emissions. In their effort to reduce the harmful effects of wastes, researchers are exploring using industrial by-products, such as red mud, fly ash (FA), blast furnace slag, and mine waste, to produce geopolymers [2–4]. Researchers are showing more interest in geopolymers because they are viable, inexpensive, and environmentally-friendly additives that can replace organic materials polymers in road construction. One benefit is a considerable reduction in the utilisation of new construction materials and the minimisation of the disposal of construction materials in landfills. The use of geopolymers leads to a green, sustainable, and eco-friendly construction that reduces the need to harvest natural resources [5]. Moreover, recycling green material waste is of great significance to civil engineers for sustainable development, which renders geopolymer a prospective future in civil engineering applications such as pervious concrete, geotechnical soil engineering, pavement engineering, and civil engineering works.

The interest in geopolymer research publication started in 1979 with an increasing number of articles on geopolymers. Figure 1 shows that the investigations on geopolymer began to intensify in the early 2000s. However, due to the growing attention to modify asphalt binder with geopolymer, it is found that the materials are able to enhance the durability and sustainability of asphalt material production and subsequently improves the economic and environmental aspects [6].

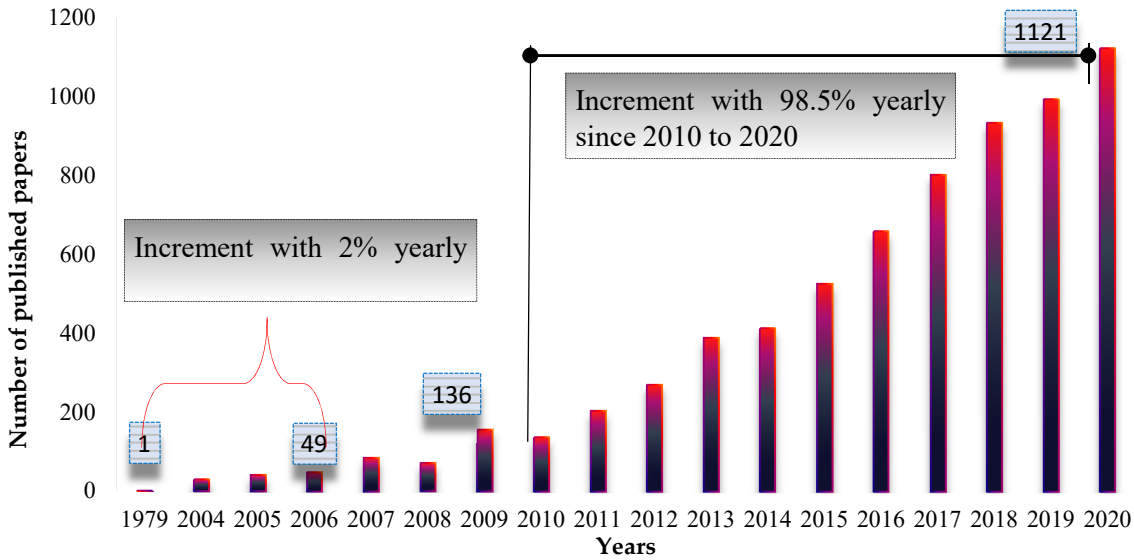


Figure 1. Annual increases in geopolymer research and publication.

There is a linear trend for the published articles on geopolymer technology between 2010 and 2020, with an increment of 98.5%. In the past year, almost 1000 articles were published in peer-review journals, which indicate the active global exploration of the use of geopolymers. This study analysed the ten-year publication trend by considering the geographical distribution of the papers published between 2010 and 2020.

Asphalt binder modification has been practised for over 50 years. The recent interest in modified asphalt binders is due to their superior chemical properties, high-temperature stability, adhesion behaviour, extended durability, and excellent mechanical strength [2]. Geopolymer-modified asphalt (GPMA) is a combination of additive or modifier used as a construction material in asphalt mixtures [7,8]. There is not much research on geopolymers during the past four decades, and the interest in geopolymers is a recent phenomenon [8].

A geopolymer material is a new replacement of conventional asphalt binders with higher strength; in the geopolymer industry, wastes have strengthened as raw materials for geopolymer preparation, such as coal gangue, FA, tailings, and slag [6]. However, the innovative use of geopolymer in warm mix asphalt (WMA) additives is expected to pave the way for using industrial wastes and reduce the asphalt-mixing temperature. Both materials are important in utilising substantial waste resources and enhancing environmental protection [6–9]. Moreover, the benefits of GMAM are lower carbon dioxide production emissions, more significant chemical and thermal resistance, and better mechanical properties at both ambient and extreme conditions.

Furthermore, the cost of producing modified asphalt is 15% to 50% lower than for conventional asphalt [9]. The cost of recycling and using geopolymers as road construction materials are relatively low [10]. Recent studies have devoted efforts to produce cleaner asphalt binder mixtures by reducing production, mixing, and compaction, temperature composites as a filler of hot-mix asphalt (HMA) that effective bitumen volatile organic compounds (VOCs) could be reduced using geopolymer additives 6% total weight of asphalt binder [11].

Several researchers have reported that the performance of geopolymer stabilised reclaimed asphalt pavement (RAP) satisfied the requirements of pavement base and subbase applications. RAP is increasingly becoming a popular material in unbound base and subbase applications due to its lower cost than natural quality aggregates. The sustainable usage of RAP also leads to significant economic savings for constructing new highway pavements [12–15]. Therefore, this study aims to provide a comprehensive review of the components, clean production techniques, heat curing methods, and properties of GMAM to provide insights into the potential application of GMAM material in different mixtures to produce WMA, RAP, and HMA.

Figure 2 shows the geographical distribution of the papers published in the previous ten years. Chinese researchers published 13% of the articles, followed by Indian (8%), Australian (10%), and American (7%) researchers. Almost half of the papers were published in Asia (47%), especially China, India, Malaysia, and Saudi Arabia, 26% were published in Europe, and 27% were published in Africa, America, and Oceania.

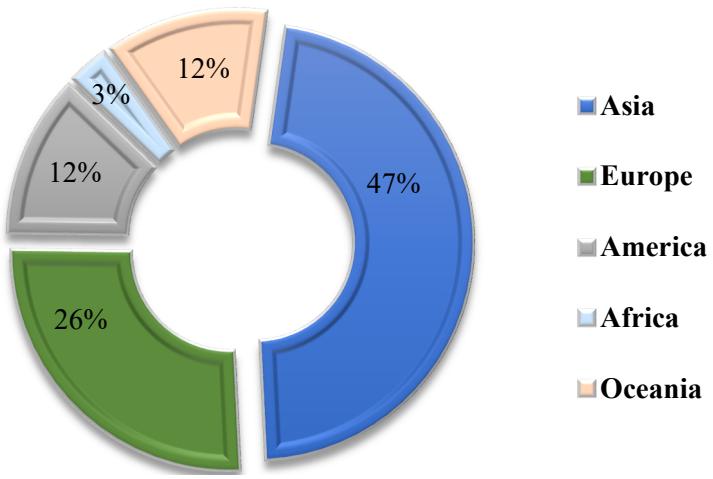


Figure 2. Geographical distribution of the published articles.

This paper presents a comprehensive review of waste-based geopolymer, including its current status, curing regimes, production method, properties, and potential uses in the pavement construction industry.

2. Geopolymer

Several researchers have explored the feasibility of using industrial by-products such as blast furnace slag and FA as precursor materials [2]. The precursor materials are inorganic polymers derived through dissolution, polycondensation, and aluminosilicate precipitation at ambient temperature. One of the benefits of geopolymers is their high compressive and flexural strengths. The manufacture of geopolymers is carried out at an ambient temperature, emits less carbon dioxide, and uses inexpensive waste materials (FA, silica fume, various types of clays, and agricultural wastes) [16]. The consistency of FA properties is non-guaranteed because of the presence of contaminants such as iron and calcium. Therefore, geopolymers are the critical resources for the future production of geopolymer asphalt [16,17]. Other precursor sources are raw material geopolymers and rocks with high aluminium oxide contents [18]. The performance-based research focused on FA-modified asphalt nature, while others focused on the kaolin geopolymer binders performance [7].

The production of geopolymer requires a chemical activator that serves as a mild alkaline reagent. It has the properties of an aqueous silicate solution that contains metal alkali and silica, with a molar ratio SiO_2:M_2O exceeding 1.65, where M is an alkali metal, either potassium (K) or sodium (Na) [19]. Figure 3 shows that any material with a high silicon and aluminium content is suitable as raw materials, which means that many materials can

produce geopolymers. Kaolinite is the initial material used to obtain geopolymers. Table 1 shows the chemical composition of geopolymers.

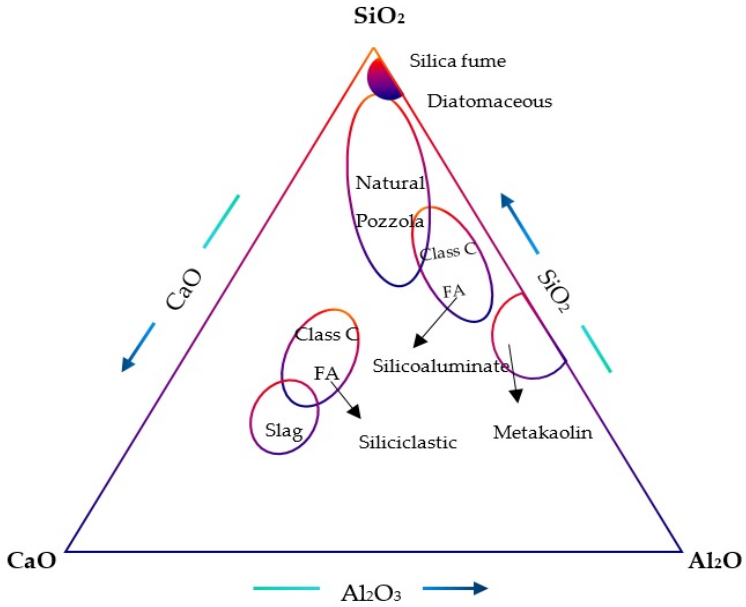


Figure 3. The ternary chemical composition of materials (SiO_2–CaO–Al_2O_3).

Table 1. Chemical composition of the different types of geopolymer (%).

Oxide	Fly ash (FA) [16]	Kaolin [5]	Metakaolin (MK) [17]	Silica Fume [18]	Alkaline Silicate Solution [19]
SiO_2	57.2	52.00	55.90	94.92	24.9
Al_2O_3	23.5	35.00	37.20	0.02	-
Fe_2O_3	3.8	1.00	1.70	1.28	-
TiO_2	-	0.90	2.40	-	-
CaO	9.3	<0.05	0.11	0.03	-
MgO	1.0	0.70	0.24	0.01	-
K_2O	-	2.00	0.18	0.15	-
Na_2O	2.43	0.05	0.27	0.28	18.5
SO_3	0.2	-	0.02	0.02	-
P_2O_5	-	0.1	0.17	-	-
Loss in ignition	-	-	0.80	-	-

2.1. Materials

The geopolymer used in asphalt binder modification is derived from various waste products. The following subsections give a detailed description of the waste materials.

2.1.1. Fly Ash (FA)

FA contains considerable amounts of silicon dioxide (SiO_2) (both crystalline and amorphous), aluminium oxide (Al_2O_3), and calcium oxide (CaO) and is the main mineral compound in coal-bearing rock strata. Preparation of FA geopolymer often involved using aluminosilicate and potassium hydroxide. Figure 4 is the scanning electron microscopy (SEM) image from the LEO Stereo-scan 440, which shows that FA's morphology consists of hollow spherical particles [20].

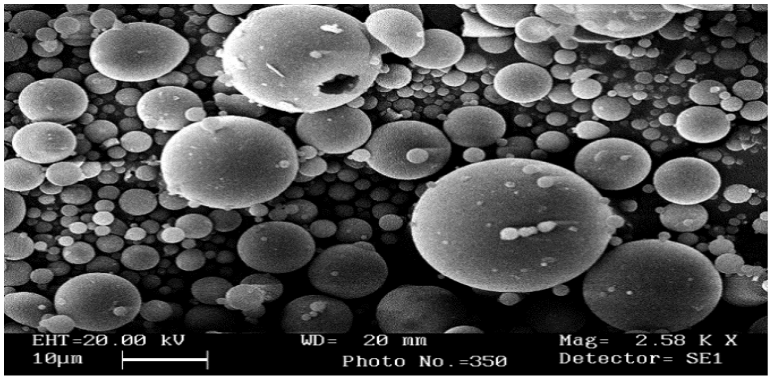


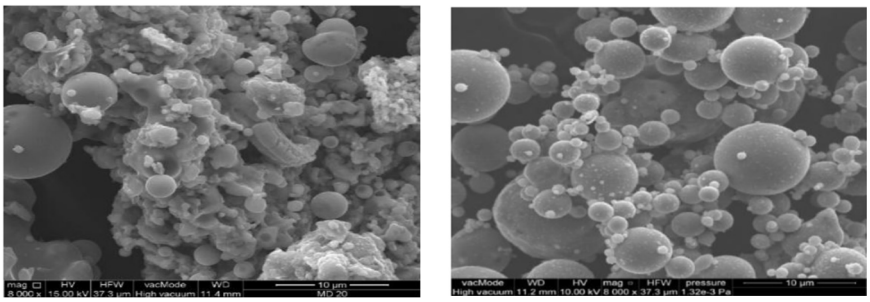
Figure 4. Scanning electron microscopy (SEM) image of FA [21].

2.1.2. Commercial Fly Ash

The commercial FA from a coal-fired power plant comprises a heterogeneous mixture of silica glasses, aluminosilicate, and a minute amount of crystalline materials that include mullite, hematite, magnetite, and quartz [22]. The inert particles are the end-products of the initial coal combustion [23]. Table 2 shows the chemical composition of class C and class F fly ash. Figure 5 shows that class C and class F FA's morphology is primarily amorphous aluminosilicate glass between 10 µm. Furthermore, the shape and morphology of SEM images at 10 µm was observed for class C FA as shown in Figure 5a,b. Hence, for class C FA, the existence of asymmetrical clusters of >10 µm, the chemical composition of which corresponded to anhydride compared to class F of FA, while in the case of the FA-C, their contribution is the much lower bulk as shown in Figure 5b.

Table 2. The chemical composition of class F and class C fly ash [25].

Materials Mass %	SiO_2	Fe_2O_3	Al_2O_3	CaO	K_2O	Nn_2O_3	SO_3	MgO	LOI
Fly ash class C	20.7	32.0	9.01	2.09	1.04	0.07	00.69	1.61	2.97
Fly ash class F	55.23	10.17	25.95	12.65	0.65	0.55	0.86	0.18	5.25



(**a**) (**b**)

Figure 5. SEM Image of Raw Commercial class F (**a**) and C (**b**) fly ash [24].

The final reaction product of alkali-activated FA is an amorphous to semi-crystalline structure similar to a zeolite precursor. The activation degree reaction of geopolymer paste is dependent on the ash materials glassy content [22].

2.1.3. Metakaolin

Metakaolin (MK), including kaolinite, is a source of aluminosilicate material. MK is manufactured through dihydroxylation calcification of kaolin clay at between 500 and 900 °C. This process chemically bonds the water and transforms a large portion of the octahedrally coordinated aluminium in the kaolin into five- and four-fold configurations [26].

MK has a small particle size, making it suitable for gloss materials [27]. Platy kaolinite particles provide an excellent coating opacity and printability. MK with a solid/liquid (S/L) ratio of 0.8 has the highest microstructure strength and a dense geopolymer matrix [28]. The presence of these minerals in MK influences the reaction steps and final properties of GPMA. It could also affect geopolymer modification due to the distinct forms and mineral composition of the MK.

2.1.4. Sodium Hydroxide (NaOH)

NaOH is an alkaline activator in the production of geopolymers. While it lacks activation level maintenance as the K^+ ion, sodium cations are comparatively smaller than potassium cations. It can migrate throughout the paste network with relative ease and increase sensitisation. NaOH has a high charge density that promotes additional zeolite formation energy. The properties of the resulting paste are dependent on the concentration and molarity of the activating solution. Chemical dissolution is accelerated by a high ratio of NaOH, which reduces the generation of carbon-hydrogen (CH) during binder formation [22].

2.2. Chemical Properties

The geopolymer comprises two components, a chemical activator and an aluminosilicate material. There are two significant properties of aluminosilicate materials, raw, rock-based materials and industrial by-products [29]. The formation of geopolymer originators is dependent on the dissolution of alumina and silicate from the initial Si-Al materials in the alkali silicate solution, where the degree of dissolution is dependent on alkali silicate concentration, the alkali silicate concentration, and the particle size of Si-Al. The catalysis of the polycondensation reaction is dependent on the alkali hydroxide. It allows the dissolution with the initial material reaction.

The geopolymer contains mainly SiO_2, Al_2O_3, Fe_2O_3, and MgO. FA, slag, MK, and silica fume are in different classes depending on the total chemical composition. MK paste activation properties with alkali solution at S/L ratios range between 0.40 and 1.20 [30]. The alkali activation solution for MK is Na_2SiO_3/NaOH. In this case, distinct ratios displayed behaviour that the S/L of 0.80 produced the highest value at the Na_2SiO_3/NaOH ratio of 0.20. The mineral content of the MK influences the reaction process and final properties of GPMA.

2.3. Morphological Properties

The geopolymer morphology analysis can give quite valuable information regarding the surface topography and composition of the sample such as Na_2SiO_3, silica fume, and NaOH concerning the size, shape, and structure of geopolymers and the relationships of their constituent parts. In contrast, three-dimensional and topographical imaging can also be obtained [10]. However, the morphological evolution of calcium-rich ESP and alumino-siliceous precursor FA based geopolymer used SEM to analysis the structure of the FA geopolymer synthesised; the geopolymer products contain various topographies: dense and bulky geopolymer binders, FA balls, pores, micro-cracks, voids, and particles listed from lower than 1 μm to more than 200 μm. FA particles are solid spheres that range from 1 to 100 μm [21]. A difference in the chemical composition of class C and class F fly ash is the calcium content, where Class C fly ash has a higher calcium content. Class C fly has between 50 and 70% of pozzolanic compounds (alumina oxide, iron oxide, and silica oxide), while Class F fly ash has at least 70%. In contrast, geopolymer mortar's flowability is reduced using GMA's high content due to the increase of non-spherical particles in the microstructure in the asphalt binder [24]. The spherical particles have the same fineness and micro size, and about 12.5% of the ash is retained in a 45 μm mesh sieve [31].

Based on the micrograph illustrated in Figure 6, FA-based geopolymer's microstructure is a porous, heterogeneous mixture of non or partly-reacted FA grains, residual alkaline precipitates, and geopolymer gel. Besides, it shows the microstructure of the FA-based

geopolymer at 12,000 magnifications [32]. Most of the particles are spherical, but some of the particles are fused. The macroparticles are called pedosphere. According to Oderji et al., the elemental data shows that more than 50% of the FA samples are amorphous alumino-silicate spheres and a smaller percentage of iron-rich spheres [30].

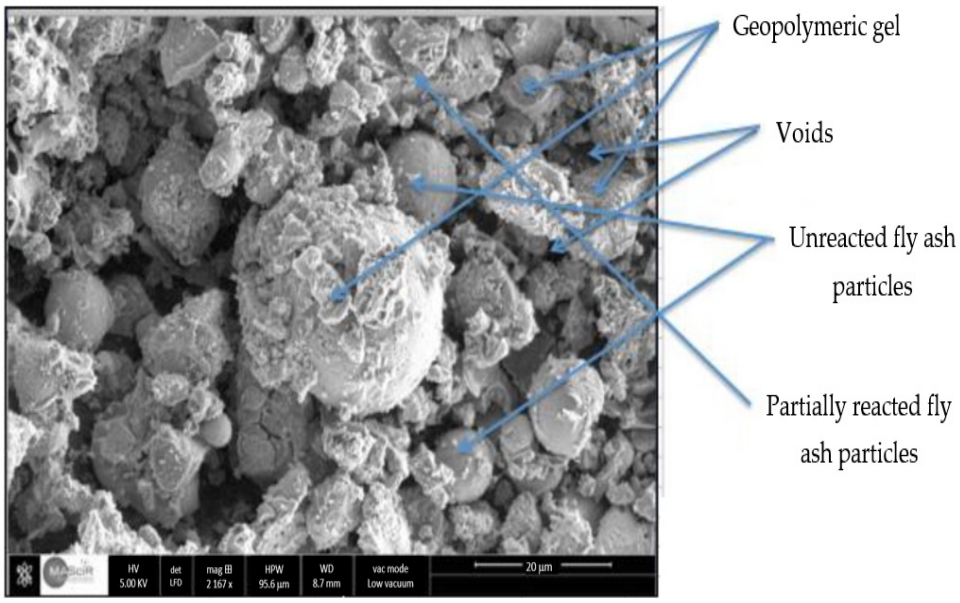


Figure 6. SEM micrographs for the FA geopolymer [32].

Most MK spots range from 1 to 20 µm. MK is a porous, angular-shaped, platy particle with a specific gravity of between 2.20 and 2.60. There is no one particular mixture that is the best for the geopolymers derived from an extensive range of sources. Essentially, MK comprises alternating buckled aluminate and silicate layers. The silicon is in a four-coordination and aluminium mixture of 6-, 4-, and 5-coordination. There are discussions on the exact function of each of the three distinct coordination states of AI in terms of geopolymer behaviour. Generally, the strain in the bonding network formed during thermal dihydroxylation influences MK reactivity [27].

The relative silica content is critical in terms of chemistry [33]. Slag alters the pore size distribution of geopolymers and gives it a rough surface texture with crystalline, platy structures. The SEM micrographs show the porous structure [34,35].

3. Characterisation of GMA

A binder is a viscous liquid that flows smoothly at high temperatures. It has the behaviour of an elastic solid at relatively low temperatures. However, some of the input energy may spread within the asphalt and cause permanent degradation (viscous behaviour) [35]. Researchers categorised asphalt binder modifiers into several key groups based on their composition, fillers, hydrocarbons, agents, polymers (elastomeric and elastomeric), fibres, and anti-stripping property. These additives have critical chemical and physical properties that influence the performance of asphalt mixture pavement. Asphalt additives reduced mixture stiffness at low temperatures and increased the stiffness at high temperatures [36–40]. Table 3 summarises the elasticity of the mixtures under ambient temperature.

Table 3. Types of asphalt, ratio, and activator geopolymers used in asphalt modification.

Author	Year	Country	Objective	Geopolymer and Ratio	Asphalt Type	Activator	Key Findings
Rosyidi et al. [2]	2020	Malaysia	Investigate the strength, chemical, morphology, and adhesion properties of geopolymers	FA class F 0, 3, 5, 7, 9%	80/100	Sodium silicate and NaOH	The optimal concentration for asphalt binder modification is 5% geopolymer.
Tang et al. [39]	2020	China, Hong Kong	Emission reduction	MK slag silica fume 0, 6%	AH-90 & PG64-28	NaOH	Reduce volatile organic compounds.
Hamid et al. [18]	2020	Canada and the USA	Distresses caused by flexible pavements	FA-Based Geopolymer 0, 3, 6, and 9%	PG58-28	Na_2SiO_3 (8 M)	Increased temperature susceptibility, shear modulus, rutting resistance, high-temperature grading reduction in CO_2, and increase the percentage of geopolymer not affecting the microstructure of the binder.
Huynh, Magee, and Woodward [14]	2020	United Kingdom	Investigate the traits of semi-flexible composite materials integrated with geopolymer grouts and RAP	Ground-granulated blast furnace slag 40,50,60, 80% FA 20, 40, 50% MK 20% silica fume 20%	RAP	Geosil, with 45% Na_2SiO_3(1.6 M) 0.27, 0.33, 0.38, 0.52	Both geopolymer grout and RAP content influenced performance. Improved performance is associated with mixtures of high-strength grout and low RAP content.
Hamid, Baaj, and El-Hakim [18]	2019	Canada and the USA	Investigate the possibility of using by-product materials	FA and glass powder 0, 4, 8, and 12%	PG58-28	100% NaOH (8 M) and 50% Na_2SiO_3	Improved fatigue resistance, rutting resistance.
Khan et al. [20]	2019	Malaysia, Kuwait	Determine the optimal dose combination of superplasticiser to fulfil the flowability requirement of grouts and optimise the compressive strength	Grouts, FA, and 1.25% recycled waste plastic (PET)	60/70 & PA 20–35%	Na_2SiO_3: NaOH (3:1) Superplasticizer 1% by FA	Eco-friendly and contribute to sustainable pavement construction.
Ariyadasa and Nataatmadja [22]	2019	Australia	Use geopolymer as a modifier	FA class FA and sodium silicate 2.5% to 6% step 0.5% by mass of RAP	Type C170	Na_2SiO_3 10 M	Further study on geopolymer as a supplementary binder in FB stabilisation with NaOH as an additional accelerator is required.
Tang et al. [7]	2018	China	Comprehensive study of WMA	MK Slag silica fume 0%, 2%, 6%, 10%.	AH-90 PG64-28	Silicon oxide, calcium oxide, and aluminium oxide	The optimum dose of geopolymer additive is 6% (by weight of the asphalt binder) and the optimum mixing temperature for WMA is around 140 °C.

Table 3. *Cont.*

Author	Year	Country	Objective	Geopolymer and Ratio	Asphalt Type	Activator	Key Findings
Hoy et al. [15]	2018	Thailand	Determine the impact of geopolymerisation once the slag is activated by alkaline activator-stabilised RAP	RAP + 20% slag-based geopolymer	RAP	NaOH: Na_2SiO_3 40%:60%, 50%:50%	The suitable S-based geopolymer-stabilised RAP can produce RAP-S geopolymers as a sustainable pavement base course and reduce gas emission.
Dayal and Soundarapandi [13]	2018	India	Evaluate the properties of FA-based geopolymer coated aggregates and their effect on asphalt mixtures characteristics	(FA1, FA2) class F 4, 4.5, 5, 5.5, 6% FA-based geopolymer coated aggregates	VG 10	FA1, at 8 M, 10 M, 12 M, 14 M, and 16 M. FA2 at 15 M, 22 M, and 29 M.	Geopolymers prepared with higher calcium content increases strength.
S.I.A Ali et al. [41]	2017	Turkey, Malaysia	Investigate the use of fly ash as a modifier. Perform tests to evaluate performance, including softening point, viscosity, and dynamic shear rheometer (DSR) tests	FA 0, 3, 5, 7%	60/70	Na_2SiO_3 and NaOH (8 M)	Improve resistance against rutting at high temperatures. The addition of 5% FA produced an optimal result.
Hoy et al. [15]	2017	Thailand and Australia	Incorporate RAP and FA in the pavement	FA 0, 20%	RAP-FA	(Na_2SiO_3), (NaOH) (10 M)	NaOH has better durability performance and formed stably cross-linked energy saving and reduces greenhouse gases emissions.
S.I.A Ali et al. [42]	2017	Turkey	Evaluate the performance of using the oscillation test	FA class F 0, 3, 5, 7%	60/70	Na_2SiO_3 and NaOH (8 M)	Enhanced viscoelastic properties of asphalt binder.
Ibrahim et al. [8]	2016	Malaysia	Investigate the physical properties and storage stability of the asphalt modified FA geopolymer	FA 0, 1, 2, and 3%	80/100	NaOH and Na_2SiO_3 (8 M)	The addition of geopolymer into asphalt binder improves permanent deformation resistance compared to conventional asphalt.
Ibrahim et al. [43]	2016	Malaysia	Investigate physical properties and storage stability	FA class F 0, 3, 5%, 7%, 9%	80/100	Na_2SiO_3	Addition of 5% FA produce optimal results.
Ismail [25]	2011	Malaysia	Investigate the creep properties of geopolymer binder mixtures	FA, HMA	80/100	NaOH Na_2SiO_3 8 M	Enhanced creep stiffness and rutting resistance.

FA = fly ash, MK = metakaolin, Na_2SiO_3 = sodium silicate solution, NaOH = sodium hydroxide, K_2SiO_3 = potassium silicate, M = molar, WMA = warm mix asphalt, HMA hot mix asphalt, RAP = reclaimed asphalt pavement.

3.1. Physical Characterisation

The modified asphalt binder was evaluated to improve its physical properties, including visco-elastic properties and durability [44,45]. The evaluation considered temperature, mixing time, and characteristics of the asphalt and geopolymer to obtain balanced and superior modified asphalt because they influence the performance of asphalt mixes (Table 4).

Table 4. Physical properties of geopolymer-modified asphalt (GPMA).

Reference	Year	Geopolymer %	Ductility cm	Viscosity at 135 °C cP	Penetration of 0.1 mm	Softening Point °C
Rosyidi et al. [2]	2020	0%	150	0.36	84	47
		3%	126	0.42	76	49
		5%	100	0.46	61	56.5
		7%	91	0.43	68	53
		9%	118	0.43	71	49.5
Tang et al. [7]	2018	0%	137.4	0.6	85.1	48.5
		2%	133.2	0.39	84.5	50.1
		6%	130.1	0.3	83.4	50.3
		10%	127.8	0.25	82.8	51.6
Ibrahim et al. [8]	2016	0%	151	0.37	86	48.5
		3%	127	0.43	78	50
		5%	101	0.47	62	57.5
		7%	92	0.44	69	54
		9%	117	0.44	72	50

The incorporation of up to 10% of weight content resulted in enhanced stability, density, flow, air voids, and asphalt mixture stiffness [2]. Future research should seek to improve high-temperature long-term storage stability without causing phase separation [17]. The GPMA mixture has a strong influence on performance due to the impact of elasticity properties. Modification of the asphalt mixture with a 10% modifier resulted in enhanced deformation [46,47].

Asphalt binder modification with geopolymer improved stability, fatigue resistance, rutting resistance, and low-temperature cracking and reduced the flow of asphalt mixture [48]. It also reduced mixture viscosity and mixing temperature and enhanced workability.

3.2. Chemical Characterisations

3.2.1. Fourier Transform Infrared Spectroscopy

Geopolymers contain several metal components such as silicon, potassium, and aluminium, making them suitable for Fourier Transform Infrared Spectroscopy(FTIR) analysis [49,50]. The two major molecular components of asphalt are the polar and nonpolar groups. The polar compounds, such as asphaltene, are responsible for the elastic properties, while nonpolar groups, such as the maltene fractions, influence the mixture's viscous behaviour [2].

Because of the simplicity of analysis and minimal preparation required for FTIR, it is an ideal analytical tool for determining the presence of solvents in asphalt [7]. All spectra are obtained with 32 scans of a 4 cm resolution in wavelengths ranging from 600 to 4000 cm^{-1}. According to Silva, asphaltenes are polar compounds with a high molecular weight [51]. FTIR spectroscopy can identify the functional and structural changes in the fraction of the binders caused by the severe oxidation process in the RTFO [52,53]. Table 5 shows the chemical composition of asphalt binders that comprises a complex mixture of mostly organic and organometallic compounds.

Table 5. Elemental composition of an asphalt binder [54].

Element (%)	Mexican	Arkansas-Louisiana	Boscan	California
Carbon (C)	83.77	85.78	82.90	86.77
Hydrogen (H)	9.91	10.19	10.45	10.93
Nitrogen (N)	0.28	0.26	0.78	1.10
Sulphur (S)	5.5	3.41	5.43	0.99
Oxygen (O_2)	0.77	0.36	0.29	0.20
Vanadium (ppm)	180	7	1380	4
Nickel (ppm)	22	0.4	109	6

Table 6 highlighted FTIR band's effect on material behaviours, which shows that the materials exhibit different behaviours. Maltenes comprise three groups: saturates, resins, and aromatics [55,56]. The saturated compounds consist primarily of branched-chain and straight aliphatic hydrocarbons, alkyl-naphthenes, and alkyl-aromatics. According to Alehyen and Zhang, the saturated compounds make up 5% to 20% of the GPMA binder. The resins, which are the strong adhesive of the binder, are made up of carbon and hydrogen with traces of oxygen [32,57].

Table 6. Wavenumber and band assignment for different materials in FTIR.

Wavenumber (cm^{-1})	FA	MK	Silica Fume	Geopolymer	Assignment
3441	√	√	√	√	OH groups of Si-OH and water molecules that are adsorbed on the FA surface
3432			√	√	OH groups of Si-OH and water molecules that are adsorbed on the FA geopolymer surface
1660				√	Stretching of H-O-H
1622	√				Stretching of H-O-H and O-H
1451			√	√	O-C-O stretching (carbonates)
1075	√	√	√		Al-O-Si and Si-O-Si asymmetric stretching
997		√		√	
894			√	√	Si-OH stretching
795	√				
771				√	Al-O bending vibration
733				√	
611				√	
558–560	√	√		√	Al-O-Si and Si-O-Si asymmetric stretching
420–500	√	√	√	√	Al-O and Si-O- bending vibration

Geopolymers can serve as asphalt binder modifiers through the wet or dry process. Rosyidi et al. employed the FTIR spectra to analyse geopolymer-modified asphalt binder and discovered a slight change in the functional groups. The aromatic C-C stretching peaks occurred at approximately 1600 cm^{-1} (stretch), 1475 cm^{-1}. The maximum stretching of the C-N amine group occurred at 1390 cm^{-1} [2]. According to Hamid et al., the geopolymer spectra at 3432, 444, and 997 cm^{-1} are the most critical transmission bands [18].

Geopolymer FA is an influential group at 1075 cm^{-1} because of the Al-O-Si or Si-O-Si unequal stretching band on the description curve compared to the other geopolymers investigated in this research the Al-O-Si bond is at the 538 cm^{-1} bands [58–60].

The geopolymer did not significantly change the FTR spectrum, which means there is no change in the functional group due to the low geopolymer percentage. The geopolymer's absorption may overlap with the asphalt binder's absorption because of the high amount of asphalt binder used [61,62].

The addition of the small amount of geopolymer (less than 3%) has a negligible effect on the modified binder's FTIR spectra [14]. However, the modifications added in temperature difference with higher than 4 °C is evidence of segregation in storage stability and is considered unstable. The long chains tend to align and flow as the load

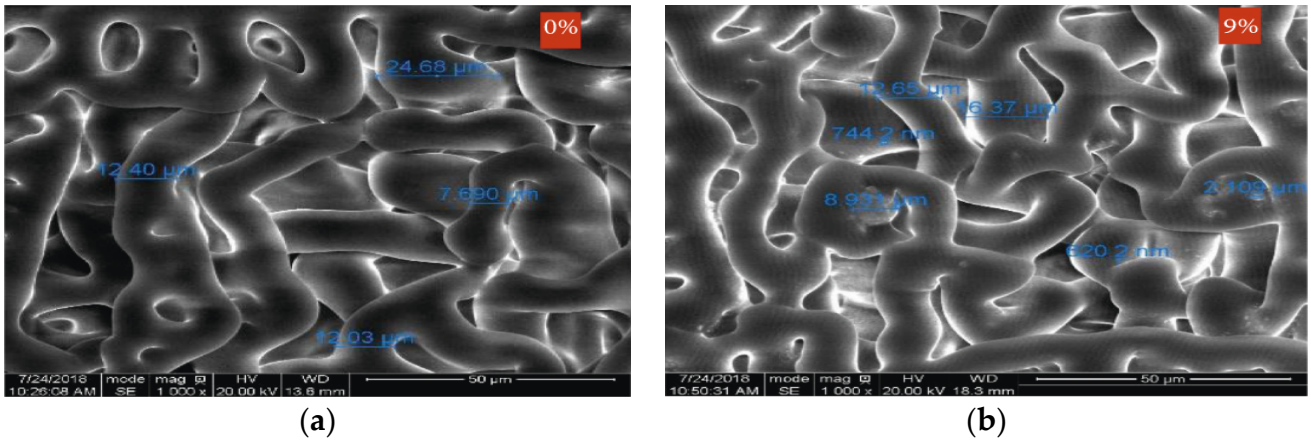
or temperature rises, which causes the asphalt to behave as a viscous liquid instead of an elastic solid. The molecules return to their initial shape (elastic behaviour) upon removal of stress or during cooling.

According to Rosyidi et al., geopolymers can release water [2]. These observations indicate that amorphous products were generated during the mixing process. Consequently, the sol converts into a colloidal gel structure [3], which resulted in better behaviour at higher temperatures in terms of permanent deformation [63].

3.2.2. Scanning Electron Microscopy (SEM)

SEM produces an image by scanning a focused electron beam across a specimen. Geopolymers are molecules comprising thousands or hundreds of atoms [17,64]. Geopolymers alter the microstructure of asphalt binders by making the network structures more coarse [15]. The denser fibril structure in the SEM image indicates a stiffer binder [13].

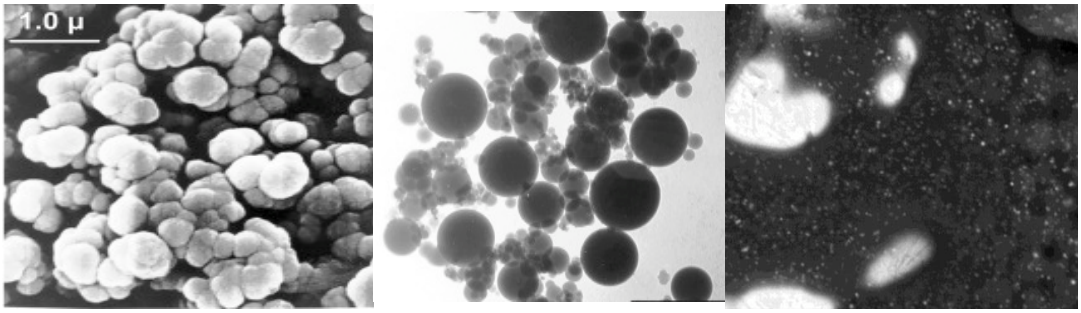
This study performed the SEM test to determine the microstructure of all modified asphalt binders. The results showed no significant difference in the fibril structure of the asphalt binders modified with 3, 6, and 9% geopolymer. Figure 7 shows that the nanoparticles are well-dispersed, and the microstructure is homogeneous without any clustering of the modifier [18]. Based on the investigation of the SEM images appears that the virgin asphalt binder 0% additive in Figure 7a compared to 9% geopolymer additive not affecting the microstructure. Thus, 9% revealed a minor effect on the ranges for modified asphalt binder geopolymer as shown Figure 7b.



(**a**) (**b**)

Figure 7. SEM micrographs of the geopolymer-modified asphalt; virgin asphalt binder 0% additive (**a**) and 9% geopolymer additive (**b**) [18].

Figure 8 shows that the geopolymer-modified binders have slightly smaller fibril diameters than the original binder. The geopolymerisation produced tiny zeolite crystals on the geopolymer surface. The crust of reaction products binds weakly to the microspheres. Such bonding between the grains is formed through chemical reactions [65]. The geopolymer particles are well-dispersed and have good compatibility with the asphalt binder. The incorporation of the geopolymer into the asphalt binder resulted in an improvement. The addition of varying percentages of geopolymer did not affect the binder's microstructure. Generally, the geopolymer enhanced the binding ability of the asphalt binders [66]. Figure 8 shows the SEM micrograph for silica fume geopolymer-modified asphalt. The particles are spherical and less than 1 µm in diameter.



(**a**) (**b**) (**c**)

Figure 8. (**a**) Silica fume, (**b**) the transmission electron microscope dispersed individual particles, and (**c**) geopolymer-modified asphalt [67].

The geopolymer-modified asphalt binders with similar physical properties could produce different SEM patterns that evolve in different ways. MK geopolymer-modified binders have significantly enhanced the structural chain characteristics and storage stability. The particle size of MK relative (1.5 μm vs. 0.1 μm) with different sizes is shown in Figure 9 [62]. The SEM image shows the morphological changes in the MK-modified geopolymer [2]. The optimum quantity for asphalt modification is five percent of the modifier.

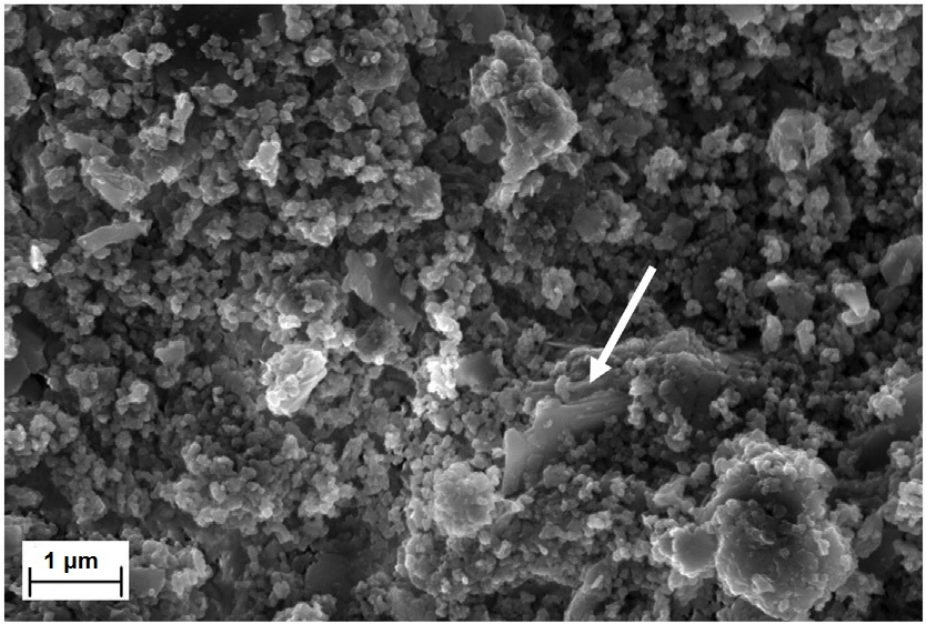


Figure 9. Micrograph of MK geopolymer [62].

The incorporation of higher geopolymer percentages could increase the asphaltene levels in the asphalt binder [5,68,69]. The enhanced binder could improve asphalt stiffness and damage resistance [70].

3.2.3. Geopolymer Binder and Reaction Mechanisms

According to Duxson, there are five steps in a geopolymer reaction. The first step is the dissolution of source material by highly alkaline ions to produce silicate and aluminate species [70]. The second step is blending the silicate and aluminate species to obtain an aluminosilicate solution. Third, the highly concentrated solution with a high pH initiates the gelation process that produces geopolymer gel. The fourth step is the reorganisation of the gel network, which forms the geopolymer microstructure and pores. The fifth

step produces the three-dimensional geopolymer added to the asphalt binder to obtain GMA [71,72].

Several factors influence the GMA: activating solutions associated with silicate concentration (SiO_2/M_2O ratio), the type of alkali metal cations, and the alkali solution (H_2O/M_2O ratio, where M is equal to Na and K). The aluminosilicate sources dissolve into SiO_4 and AlO_4 tetrahedral units involved in the polycondensation process, as displayed in Figure 10 [73].

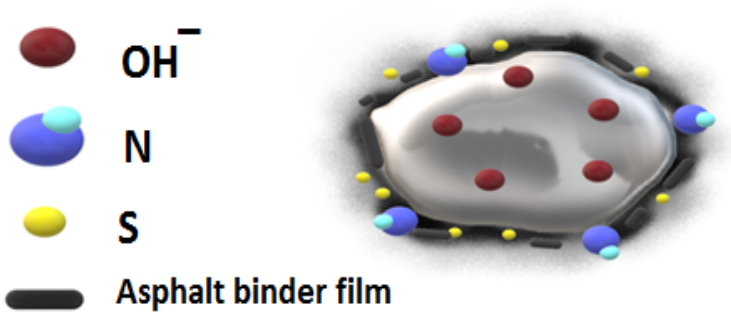


Figure 10. Interaction in the geopolymer modified asphalt.

Geopolymers can form in systems with low Si/Al ratios, elevated curing temperatures, or where Li^+ is the alkali cation with or without the presence of amorphous [41]. The curing conditions' factors such as curing duration, humidity, and temperature affect geopolymer's strength [10,74]. However, the critical difference between GPMA and other asphalt modifiers is the geopolymer component. The aluminium and silicon oxides exist in FA, slag, silica fume, and MK in geopolymer, improving geopolymer-modified asphalt binder performance. Moreover, the geopolymer binds the loose coarse aggregates and other materials such as the filler. The properties and amount of the component materials determine the viscoelasticity and strength of GPMA. Storage stability is how easily the GPMA can be consolidated, transported, and placed without losing homogeneity or stability. It is dependent on the features of asphalt's modifiers affected by the consistency and the materials in the GPMA [60].

However, the casting of GPMA in actual construction requires particular attention to enhancing the asphalt pavement in terms of permanent damage, water surface tension, compatibility, homogeneity, and workability of both the asphalt binder and asphalt mixture. These parameters are affected by the binder's shape, modifier, aggregates, mixing, particle size, and distribution [6,15,75].

3.3. Rheological Properties

Pilehvar et al. investigated the rheological parameters of complex modulus and phase angle. The microcapsules with a hydrophilic shell increase the elasticity and stiffness of the geopolymer-modified binder [76]. Geopolymer increased the failure temperature, viscosity, elastic modulus, and complex modulus and enhanced the binder's rutting resistance (Figure 11). The incorporation of higher percentages of geopolymer resulted in improved performance where binders modified with up to 8% high-purity quartz silica fume performed better than the unmodified asphalt binder [77]. The modifier constituents influence the viscoelastic properties of the asphalt binder [5].

According to Golestani et al. [76], modifiers can enhance the storage stability and the rheological properties of binders [78]. The addition of 5% of geopolymer FA with asphalt binder is able to resist stresses, strain, and better performance at high temperatures [3,44,45]. In addition, it is also able to enhance rutting resistance compared to conventional asphalt [79].

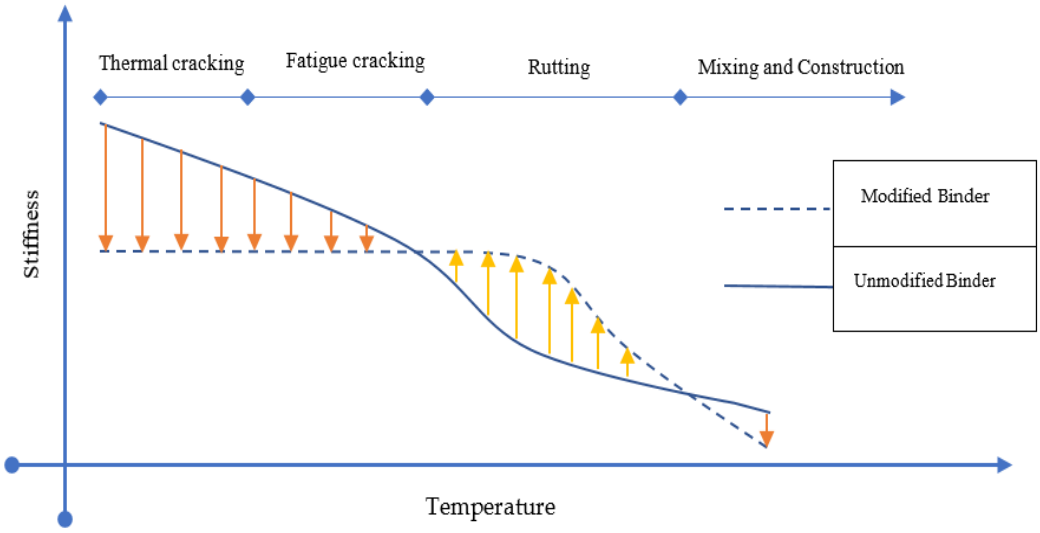


Figure 11. Improvements of geopolymer modifiers [79].

The phase angle (δ) ranges from 52 °C to 77 °C in lag between the applied shear stress and the causing shear strain [38].

Rosyidi et al. observed that the incorporation of 9% geopolymer resulted in a marked increase of 8.58% in temperature susceptibility, higher shear modulus, and lower phase angle [2]. The addition of the same amount of geopolymer by mass of binder at 10 rad/sec and 58 °C resulted in an 86.6% increase in the rutting relative to the unmodified binder. Several comparative studies found that the geopolymer behaviour proceeds better enhancement than conventional modifiers and materials, and that the geopolymer reaction products are less affected by shear forces [42,80–82]. However, many of the previous studies focused on the impact of geopolymer-modified asphalt under high temperatures by testing the rheological and rutting properties [5,55,76]. Results show that using geopolymer results in improving modified binder resistance to permanent deformation at high temperatures. Studies by [75,77] had investigated the impact of geopolymer on modified binder under low temperature. A study by [75] had investigated the ductility at the low temperature of 5 °C, and results showed significant improvement of the rheological properties in terms of improving the complex shear modulus and phase angle. A similar trend has been found by [77] as using Bending Beam Rheometer BBR test at −12 °C showed that the modified binder was less susceptible to low temperature cracking. Generally, geopolymer modification of asphalt binders resulted in significantly enhanced asphalt binder properties [2,13,14,73,76,83,84]. However, asphalt binder modification with <0.2% geopolymer has an insignificant impact on binder properties. This study recommends adding a relatively high percentage (>1.0%) of geopolymer for modifying the asphalt binder.

4. Performance Characteristics of GMAM

It is well known that the conventional asphalt materials do not meet the performance requirements for road construction that are constantly subjected to heavy loads, frequent stresses, heavy traffic, and various climatic and environmental conditions. Therefore, the asphalt materials must be modified using a suitable alternative to achieve the required properties that allow the pavement to withstand the stresses and distresses [79]. The modifier used in a specific project is determined by various factors, such as construction ability, availability, cost, and expected performance [23,85,86]. Relative to the existing additives for asphalt mixtures, geopolymers can reduce permanent deformations by more than 40% and are energy-efficient and eco-friendly. The significant microstructure enhancement during the mixing produced a new material with a different microstructure [81].

The addition of modifiers to asphalt binder mixtures increases binder stiffness at high service temperatures and thus resists rutting. Modifiers can produce softer binder

mixtures at low service temperatures, minimising thermal cracking and improving the asphalt pavement's fatigue resistance [87]. Previous studies have shown that asphalt binders do not have excellent properties in heavy loads and high or low-temperature conditions [42,81,82,88]. It is softer in the high-temperature regions and more brittle in the cold temperature regions. Stiffer asphalt binder mixtures are more resistant to permanent deformation. Geopolymer modification of asphalt mixtures increases the mixture's elasticity and stiffness in hot climates [72,73] and enhances its elastic and engineering properties [3,89].

The current research on using geopolymer as a pavement material seeks to determine the feasibility of using waste materials as sustainable economic and environmental solutions [83]. Several studies have successfully used geopolymers to modify the material in asphalt applications. Most geopolymer-modified mixes meet the minimum strength criteria for high-volume roads [83].

Many researchers have investigated geopolymer properties in road applications to determine the standard design mixtures for GMA and reduce the need for high-temperature curing. Future research should investigate the long-term durability of GMA. Future research should also identify the environmental and economic benefits of using waste materials to produce GMA [2,13,14,76]. Geopolymers can enhance mechanical properties, damage resistance during operation, and reduce greenhouse emissions and energy consumption. Geopolymers can absorb toxic chemicals and reduce deformation in asphalt mixtures by up to 81% [25].

Higher geopolymer percentages and longer curing time can improve failure temperature, viscosity, and complex shear modulus. These have the effect of enhancing the rheological properties of asphalt binders. A higher geopolymer percentage also improved rutting resistance [18]. The increase in the failure temperature of asphalt binder modified with 9% geopolymer is 8.58%, 14.2%, and 15.2% for curing periods of 2, 7, and 14 days. The incorporation of geopolymers of less than 5% has an insignificant impact on the mixing and compaction temperatures. However, a significant increase was observed in the compaction and mixing processes when asphalt mixtures are modified with 5% of FA geopolymer [14,16,40].

The particles are well-dispersed in the binder. The incorporation of higher percentages of geopolymer did not change the binder's microstructure. Furthermore, the GPMA shows remarkable fatigue-cracking resistance in HMA, WMA, and RAP [19,22,23,38].

Geopolymer-modified asphalt mixtures have low viscosity and resilient modulus. Modified asphalt mixtures have lower stiffness and density than the unmodified asphalt mixture [19,20,42]. Geopolymers satisfy the specifications set by the national road authority and are a suitable additive material for road constructions.

5. Environmental and Social Benefit

The environmental benefits of incorporating geopolymers in asphalt binders and asphalt mixtures include reduced emissions and fuel consumption because of the reduced extraction and transportation of virgin materials, reduced demand for non-renewable resources, and reduced landfill space used for the disposal of the used pavements. It also has a beneficial economic impact in developing countries where governments have to allocate a substantial budget to improve road infrastructure. [85]. The production of asphalt mixtures consumes a large amount of energy and releases CO_2 into the atmosphere. Other raw materials contain minerals, and their usage for industrial production may be regulated by environmental threshold values [86]. Among the environmental benefits of using geopolymers are reduced demand for non-renewable resources and less extraction of virgin materials [90,91]. Other methods for improving the sustainability of asphalt mixture materials include using recycled geopolymers and improving asphalt mixtures durability.

The proposed treatment and synthesis of geopolymers such as zeolite involved environmentally friendly processes that do not require elevated pressure and temperature. Geopolymer sorbents can be synthesised utilising waste products, such as slags and FA [15].

In recent years, there is an increasing global effort to improve asphalt characteristics by using geopolymers and waste materials [85]. One study has shown that incorporating 15% geopolymer into asphalt mixtures reduces fossil fuel consumption, total cumulative energy requirement, and climate change by 13 to 14% [92].

6. Economic Benefit

Geopolymer additives are produced at ambient temperature using industrial by-products to offer economic savings relative to conventional asphalt binder-based systems. The result of an analysis of life cycle costs by Dunmininu et al. showed that asphalt pavement binder is the most expensive component of asphalt pavement construction [93]. The life cycle cost analysis (LCCA) evaluates the economic implications of selected geopolymer materials on pavement construction in its design life [94]. Hoy et al. (2016) investigated Toxicity Characteristic Leaching Procedure (TCLP) and found that there is no environmental risk for RAP-FA geopolymer as pavement base layer [78]. Li et al. (2019) and several other researchers used FA as an alternative material to modify the conventional aggregates, a dynamic approach to reduce pavement cracking by developing the slow and expansive road-based stabilisers to recompense the shrinkage of road base materials [95]. The United Kingdom (UK) has limited the use of coal fuels for electricity generation. Only 1.6 million metric tons of FA were generated in the UK in 2016, a 70% decrease from the amount produced in 2012. As of 2017, only 2% of the overall electricity consumption is from coal. Despite these efforts, 30–50% of FA are sent to landfills. The United Kingdom expects to cease using coal by 2025. Bakare et al. (2019) reported that, since 2017, India has been producing approximately 196 million tons of FA annually with a utilisation rate of almost 70% [96]. However, only 55% of the estimated 5.5 Mt/a FA produced in the power plants are used in various applications as general filler, grout, concrete additive, blocks, hydraulic binder, and the remaining 45% is transported to landfills [97]. The use of 20% FA geopolymer with RAP is economically viable for pavement-based applications.

7. Conclusions

This paper presents a comprehensive review of asphalt pavement construction based on the feasibility of using geopolymer asphalt modifiers for environmental, economic, and laboratory studies for the road construction industry.

The literature review revealed that more research has to be carried out to optimise the formulations for GPMA with enhanced properties. There have to be specific standards to increase the use of geopolymer in asphalt pavements. The following conclusions are drawn.

1. Geopolymers are a critical determiner of asphalt binder properties. Modification of asphalt binders with a high geopolymer percentage resulted in higher asphaltene content. It also resulted in enhanced rheological properties and physical properties of the modified asphalt binders. The incorporation of an optimal geopolymer percentage can reduce asphalt binder viscosity. Geopolymers can improve the workability of asphalt mixtures and reduce their mixing temperature.
2. Geopolymers can improve asphalt mixture's stability, fatigue resistance, rutting resistance, low temperature cracking, and reduce flowability.
3. The road construction industry has to increase the use of more environmentally friendly materials to ensure sustainability. Geopolymers are synthesised from waste products such as red mud, FA, mine waste, and blast furnace slag. The geopolymers in asphalt pavement materials provide a sustainable way of managing waste products. Geopolymers derived from slag, MK, and silica fume can reduce gas emissions and are suitable for hot and warm asphalt mixtures.
4. The currently available technologies and practices limit geopolymer utilisation in road construction because of the heat curing requirements for achieving adequate asphalt mixture properties.

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