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Production of the Traditional Organic Mortars of Padmanabhapuram Palace—A Characterization Study on the Simulated Mortars for Their Compatibility

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Abstract: The scientific investigation performed on the different mortar typologies of the Padmanabhapuram Palace mortars in a previous study led to the formulation of a similar traditional mortar. The outcome of the study was an increase in the carbonation action and mechanical strength of the mortar compared to conventional lime mortar, primarily due to the fermented organics such as aloe vera, cactus, kadukkai, hibiscus, jaggery, and neelamari. The transformation of portlandite crystals to calcite, along with the early developed C-S-H and C-A-S-H hydrated products reported by the XRD analysis. The bio-organic spectral peaks for compounds such as carbohydrates, polysaccharides, and fatty acids were observed in the FT-IR investigation, which corroborates the XRD mineralogical results. The calcite decomposition is detected in the TGA analysis in the temperature range of 700–750 °C, with a maximum weight loss of approximately 35–37% for the aloe vera lime mortar. The addition of fermented organic extracts to the extent of 5% was found to increase the internal and external carbon absorption of the aloe vera and cactus mortars compared to conventional lime mortars. The mechanical strength of the organic lime mortar reported as 2.5 MPa, and 1.5 MPa for the reference mortar. The carbonation and hydraulic reactions due to the presence of polysaccharides, fatty acids, carbohydrates, and proteins in the formulation enhanced the compressive strength of the compatible mortar. The prepared compatible mortar will support the revival of the 400-year-old practice of the application of Palace mortars.

Keywords: ancient recipe; fermented organics; repair mortars; strength; sustainable production

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1. Introduction

Lime mortar is one of the oldest types of known mortars, and its use in construction has been debated for 10,000 years, primarily in India, Italy, Greece, and Egypt [1]. Calcium carbonate is the most common binder component, together with a hydraulic binder, and sand is usually the major aggregate phase, according to the significant number of research studies [2]. The majority of the research has focused on the use of organic chemicals in mortar paste for a variety of purposes and for modifying the properties. In comparison to other countries, India improved the strength and durability of lime mortar by using plant and animal extracts instead of pozzolan [3–5]. According to the literature, various natural organics such as curd, jaggery, cactus extract, bel pulp, lentils, and margosa oil were added to lime mortar. Blood, egg white, fig juice, gum arabic, seaweeds, and other organic mucilage have all been used to modify lime and earth mortars throughout the world. Though the precise role of natural organics is unknown, they would have been added to improve the strength and other properties of lime mortar. Arcaloa et al. [6] discussed that the historic structures should be replaced with similar original materials to protect the structure from structural distress and damages. The combination of traditional concepts with modern structures is found to be more appropriate. Recent research on historic mortars has led to the use of geologically available natural additives to modify qualities such as workability, retarders, accelerators, water repellence, and binding properties in response to environmental and construction demands [2]. A classic example is Mohenjo-Daro, an Indian heritage monument, which comprises prehistoric Indian lime mortar structures that are more than 4000 years old [4].

Lime mortars are conventionally made by combining the lime, water, and aggregate with a range of optimum organic additives (0.1–10%) to alter the qualities of the blend. Organic additions to lime mortar (oils, fatty acids, plant extracts, animal glues, eggs, blood, beer, casein, fruit juices, and sticky rice) influence the pore structure and setting time of the mortar [7–13]. Polysaccharides (found in mucilage and other plant extracts) affect the pore size distribution of lime pastes and mortars, as well as their strength and carbonation rate [4]. Proteinaceous materials (such as animal glue and blood) improve the mechanical strength and carbonation rate, and oils affect the microstructure of lime pastes and mortars by altering the carbonation pathway. Thirumalini et al. [4] investigated the effects of organic additives such as oonjalvalli (*Cissus glauca Roxb*), pananchikaai (*Cochlospermum religiosum*), kulamavu (*Persea macrantha*), gallnut (*Terminalia chebula*), and palm jaggery on the lime matrix and evaluated the mechanical strength and pore structure formations.

Experimental analysis of the mortar mix with the addition of polysaccharides and carbohydrate-rich herbal extracts qualitatively improved the mechanical properties of the lime mortar. Furthermore, the presence of carbohydrates and proteins in organics was the reason for the improved strength and durability; in fact, it has also been proven that these chemical components aid in improving the internal cohesion between the crystalline particles in lime mortars [11–15]. Specimens of lime mortars with an additional 2.5% of fresh mucilage extracted from aloe vera, *Cylindropuntia californica*, *Opuntia* engelmannii, *Opuntia Ficus-indica*, and *Salvia hispanica* mucilages produced a higher extent of bio-receptivity than the control mortar. The presence of carboxylic groups is significant because they react with divalent cations to generate an egg-box structure that allows plants to retain water. They also contain mono and divalent cations, minor proteins, and phytomolecules such as polyphenols as supplementary components. Because of its chemical composition, mucilage is an ideal lime additive, as it may prevent surface fractures in mortars while maintaining the desired moisture level [15–19].

Modern diagnostic techniques have enabled the identification of a wide variety of natural products used in historical mortars; for example, animal glue, lipids, and proteinaceous materials have been discovered in mediaeval mortars in Southern Italy, while egg white, plant juice, drying oil, and molasses have been discovered in mortars from the Spanish Colonial Period in the Philippines, and blood, crop flour, and sticky-rice have also been discovered [12].

In general, herbal extracts are similar in that they all contain polysaccharides and fatty acids. However, some differences are observed in the characteristics of each type of extracts, such as consistency and plasticity properties. The characterization study performed on historic mortars has reported that the type of lime is hydraulic, with mix proportions adopted as 1:3 for wall plasters identified by acid digestion analysis. The present study focuses on replicating the traditional mortar of Padmanabhapuram palace, Kerala. This study will surely benefit state archaeology, NGOs, and modern conservators throughout India for protecting ancient structures.

Background of Padmanabhapuram Palace

The Padmanabhapuram Palace is located on Kanyakumari Road, 55 kilometers south of Thiruvananthapuram and two kilometers east of Thuckalay, at latitude 8.2507° N and longitude 77.3267° E. The Palace, which is 400 years old, was constructed in the 16th Century and comprises 6.5 acres of 14 complex, inbuilt forts that are spread over 186 acres of land [13].

2. Materials and Methods

The hydraulic nature of the lime is established by XRF analysis and IS 712-1984 specification. The powdered samples of Dhone hydraulic lime, with an average particle size of 63 µm, were analyzed using a Rigaku ZSX Primus 1V X-Ray fluorescence spectrometer for their chemical composition (Table 1) [13]. Since the availability of standard lime is rare in the market in India, the lime was procured from a quarry. The nature of the lime used in this study is eminently hydraulic lime.

Table 1. Chemical composition of the hydraulic lime.

Sl No.	Oxides	Percentage (%)
1	CaO	55.5
2	SiO_2	30.2
3	MgO	0.98
4	Al_2O_3	6.26
5	Fe_2O_3	3.89
6	K_2O	1.97
7	Hydraulic Index	0.71
8	Cementation Index	1.66

The hydraulic index (HI) and cementation index (CI) are calculated as per Equations (1) and (2), respectively. The identification of lime based on the hydraulic index range developed by Eckel (2015):

If (1)

$0.30 < HI < 0.50$—weakly hydraulic
$0.50 < HI < 0.70$—moderately hydraulic
$0.70 < HI < 1.10$—the higher the index, the greater the hydraulic properties

The classification of lime based on the cementation index developed by Eckel (2015) is:

If (2)

$CI < 0.15$—air lime
$0.15 < CI < 0.30$—sub-hydraulic lime
$0.30 < CI < 0.50$—weakly hydraulic
$0.50 < CI < 0.70$—moderately hydraulic
$0.70 < CI < 1.10$—the higher the index, the greater the hydraulic properties

Well-graded river sand, free from organics, was used as fine aggregate in the production of the lime mortar. The lime-to-aggregate ratio was taken as 1:3 by weight, as per the Indian codal provisions IS 712-1984 [20] The aggregate grain size range was < 1.18 mm, indicatative of the coarser grains used in the production of the similar original mortar.

In India, the traditional practice was to mix through a pug mill, and the same method of operation was performed in the present study, as shown in Figure 1. The pug mill has dual iron-made rollers to crush materials with an overall rotation of 650 rpm and specific fuel consumption of up to 300 g/kWh. The instrument was procured from the UK. The mortar proportions were measured based on the consistency test, i.e., the mortar on the back of the trowel would not fall from a height of 0.5 m. The lime to organic ratio of the mix was adjusted to 0.68–0.74 for individual herbs by utilizing the flow table, which was determined according to the number of bumps required to achieve a spread value of 190 mm, a requirement for workability [13]. The prepared lime putty and sand were ground to a plastic mix condition to achieve the desired homogeneity of the mix. To experiment with the strength of the organic lime mortar, the mixtures were filled into non-corrosive molds measuring 50 × 50 × 50 mm and allowed to air cure for 28 and 56 days, respectively (IS 6932 Part (VIII) 1973) [21].

Figure 1. Traditional pug mill mixer.

2.1. Preparation of the Organic Lime Mortar

2.1.1. Preparation of the Traditional Organic Herbs

The organics were processed by fermentation using traditional methods. Approximately 3 kg each of kadukkai seeds, neelamari leaves, aloe vera, cactus, jaggery, and hibiscus flowers were taken and crushed separately. The crushed herbs were mixed with 60 litres of water and allowed to ferment for 15 days. The fermentation process was completed under aerobic conditions, i.e., the entire slurry was kept in an open area for biomineralization action. Fermentation aided in breaking the complex compounds into simple ones for better interaction. The ancient practices did not follow the standards; hence, approximate proportions were used for the preparation, as set out in Algorithm 1 [4].

Algorithm 1. Description of the lime mortar mix proportions.

```
1.  1 part lime + 3 parts aggregate + water (0.65)
2.  1 part lime + 3 parts aggregate + fermented organic water (Terminalia chebula—kadukkai)
    (KLM) (0.68)
3.  1 part lime + 3 parts aggregate + fermented water (Cactaceae—cactus) (CLM) (0.68)
4.  1 part lime + 3 parts aggregate + fermented water (Rosa Sinensis—hibiscus) (HLM) (0.74)
5.  1 part lime + 3 parts aggregate + fermented water (Asphodelaceae—aloe vera) (ALM) (0.68)
6.  1 part lime + 3 parts aggregate + fermented water (jaggery) (JLM) (0.74)
7.  1 part lime + 3 parts aggregate + fermented water (Indigofera Tinctoria—neelamari)
    (NLM) (0.68)
8.  1 part lime + 3 parts aggregate + fermented water (kadukkai + jaggery) (KLJM) (0.66)
9.  1 part lime + 3 parts aggregate + fermented water (kadukkai + jaggery + aloe vera)
    (MLM) (0.68)
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2.1.2. Organic Lime Preparation

The slaked lime was sourced from the Dhone in the Kurnool district of Andhra Pradesh, and well-graded, organics-free washed river sand was used. The ancient traditional ratio of 1:2 was adopted for the mix, according to Vitruvius' *Ten books of Architecture* [22], but this was later modified to 1:2.7 (Gotti et al.) [23]. Based on the recent application and stability factors on restoring the traditional mortar, a revised ratio of 1:3 was chosen as the simulation mortar, with added regional organics, for Padmanabhapuram Palace [14].

In India, the traditional practice was mixing through pug mill, and the same method of operation was performed in the present study, as shown in Figure 1.

2.1.3. Mix Proportions of the Organic Lime Mortar

Several combinations of lime, sand, and fermented organics with various bio-molecule components (fatty acids, carbohydrates, polysaccharides, and proteins) were formulated following the traditional process used at Padmanabhapuram Palace in Kerala (Algorithm 1). A reference mortar to compare to the compatible mortar was also prepared. The organic fermented water was added in a similar ratio of 0.65 by weight of lime as compared to the reference lime mortar [13].

2.2. Characterization Study on the Palace Mortars

The restoration mortar was prepared based on the inputs derived from the characterization study on Padmanabhapuram Palace [13]. As set out in Table 2, in the previous scientific study performed on the palace mortars, three mix proportions for three different mortar typologies were identified, namely, wall plaster as 1:3, bedding mortar as 1:2, and wall mortar to be 1:1. These mix proportions were confirmed by acid digestion analysis of the collected mortar samples. Investigation through FTIR on the material returned the peaks corresponding to the wavelength bands of polysaccharides and carbohydrates present in the organics. Similarly, the TGA analysis validated that the decarbonization of the mortars occurred at 705–730 °C. From the overall investigation, it was concluded that the type of lime was eminently hydraulic lime, supported by IS 712-1984, the particle size of the aggregates ranged between 1.18–2.36 µm, and partial grounding could have been performed on the various mixed proportions [21].

Table 2. Binder/Aggregate (B/Agg) ratio for palace lime mortars (Source: Shivakumar et al., 2020) [13].

Type of Mortars	Samples	Initial Weight (gm)	Acid Loss (gm)	Weight Retained after Acid Loss (gm)	Sand Retained (gm)	Binder Retained (gm)	B/Agg Ratio	Ranges
Wall	S1	30.5	7.75	22.75	15.5	7.25	1:2.5	**1:3**
	S2	25.8	3	22.8	16.45	6.35	1:3	
	S3	25.2	5.87	19.33	14.35	4.98	1:3	
Bedding	S4	28.4	2.34	26.06	18.56	7.5	1:2	**1:2**
	S5	15.3	4	11.3	6.62	4.68	1:2.5	
Flooring	S6	10.3	1.7	8.6	4.35	4.25	1:1	**1:1**

2.3. Mechanical Strength

The low-capacity universal 8801 Instron dynacell machine tests with a loading rate of 50 N/s were performed on 8 samples for each mix. Overall, 72 mortar cubes were cured for 28 and 56 days, respectively, to determine their mechanical strength, according to IS 6932 (Part VII)-1973 (Indian Standards 1973) [21].

2.4. Carbonation Test

The carbonation test was performed according to Rilem (1988) and UNI EN 14630-2007 [24] (Figure 2). The mortar cubes were split and sprayed with 1% phenolphthalein ($C_{20}H_{14}0_4$) in alcohol, an indicator solution, during the carbonation process. In titrations, phenolphthalein is frequently used as an indicator; it turns pink in basic solutions (a pH of greater than 8.5) and is colorless in acidic solutions. On mortar specimens, this carbonation method captures the color change boundaries between uncarbonated, partially carbonated, and fully carbonated (pH 9) regions. The test was performed on all the organic lime mortars for 28- and 56-day cured samples, and photos of the observed color changes were taken [25].

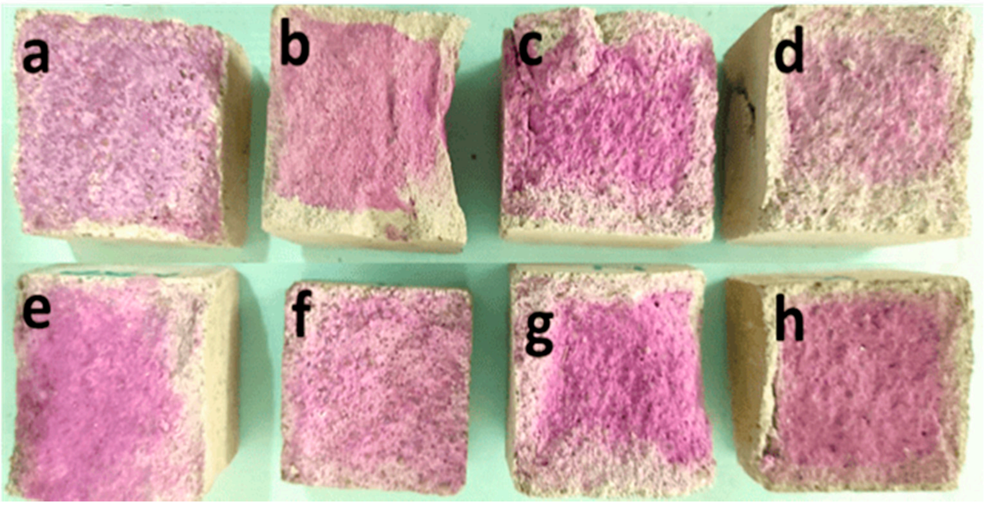

Figure 2. Carbonation tests on organic lime mortar samples: (**a**) kadukkai lime mortar; (**b**) cactus lime mortar; (**c**) aloe vera lime mortar; (**d**) hibiscus lime mortar; (**e**) jaggery lime mortar; (**f**) neelamari lime mortar; (**g**) K + J lime mortar; and (**h**) mixed lime mortar.

2.5. Analytical Investigations

2.5.1. X-ray Diffraction

Finely ground samples of 75 µm were subjected to XRD analysis. Furthermore, mineral identification was completed using a Rigaku smart lab II diffractometer with a 9 Kw and 9 mA operating system and directed sample holders made of polymethyl methacrylate or Si with diameters of 25 and 20 mm, respectively, depending on the amount of specimen used (0.5 and 0.16 m^3). Cu-Ka radiation is the energy frequency with a wavelength of 15.40 nm in a nitrogen setting and a scanning rate of 10/minute from 5° to 90° (2 h) in steps of 0.05° (2 h). The analysis yielded the XRD patterns that were used to estimate possible minerals in the historic mortar samples. Interpreting the peak positions for understanding the mineral structure was supported by the Joint Committee of Powder Diffraction Standards-International Centre for Diffraction Data (JCPDS-ICDD) by a process of phase review [13].

2.5.2. FT-IR

A sample of 5 mg of the finely ground organic mortar was made into a pellet with KBr and analyzed in the wavenumber ranging between 4000–400 cm^{-1} with 32 scans and a resolution of 0.5–16 cm^{-1} [13].

2.5.3. TGA-DTA

A Perkin Elmer Pyris-1 instrument was used to perform a thermal gravimetric analysis (TGA) of the organic mortars. A sample of 2 mg was placed in a pierced aluminum pan for examination. The experiment was performed in an inert atmosphere of nitrogen (non-oxidizing agent) with the specimen heated up to 1200 °C from room temperature with a gradient of 100 °C per minute. TGA measures mass losses, while DTA measures modifications in the structure, melting, and disintegration of materials [14]. The release of hygroscopic water (10–120 °C), structurally bound water (120–400 °C), $MgCO_3$ decarbonation (400–550 °C), and $CaCO_3$ decarbonation (600–800 °C) are the main causes of weight loss below 120 °C. The hydraulic properties of the mortars were evaluated by dividing the total amount of carbon dioxide and water (CO_2/H_2O) by the total amount of carbon dioxide and water [26].

3. Results and Discussions

3.1. Influence of Organic Additives on the Mechanical Strength of the Lime Mortar

Table 3 shows the results of the compressive strength tests for the organic and reference mortar specimens at 28 and 56 days of curing, respectively. On the 56th day, the reference mortar's strength was measured to be 1.81 N/mm^2. The compressive strength of the lime mortar with various added organics such as kadukkai, jaggery, and an aloe vera mix ranged between 1.68 and 2.76 N/mm^2. Kadukkai, a fat-rich (-COO) compound (anions), was reported to form hydrophobic salts, for example, $Ca(C_{XX}H_{XX}\text{-}COO)_2$, in the presence of a cationic Ca $(OH)_2$ suspension. Additionally, the dissolved CO_2 in the lime suspension forms carbonate ions $(CO_3)^{2-}$, which react with calcium ions $(Ca)^{2+}$ to form calcium carbonate [27]. The fermented organics were chemically active, thus contributing to re-carbonation in the conversion of portlandite to complex C-S-H creation and C-A-H during the early phases of high mortar strength production [28]. Due to a greater carbonation rate compared to the reference mortar samples, the interaction of lime and organics in the mortar contributed to a higher mechanical strength. The polysaccharide-rich cactus extract is a binder that prevents the lime mortar from drying out too quickly, resulting in a crack-free structure [29]. The polysaccharide and carbohydrate-rich combined organic (kadukkai + jaggery + aloe vera) mortar mix boosts the adhesive property between the particles to activate the calcium ions, generating calcium carbonates. Hibiscus extract contains fats, acids, flavonoids, carbohydrates, proteins, and minerals [30]. These phytomolecules in the hibiscus lime mortar mix raised the carbonation level, as evidenced by a 15% weight loss at 600–800 °C on the 56th day of the thermal study. Calcium hydroxide has been converted to calcium alkoxide and calcium carbonates, as polysaccharides in organics have changed into alcoholic components and carbon dioxide. When aloe vera mucilage (which has a good moisturizing property) reacts with lime, the polysaccharides (tannins, flavonoids, and alkaloids) undergo structural alteration, which promotes better binding and mechanical strength [15]. Further, the hydrophobic nature of proteins in aloe vera is utilized to reduce water absorption, limiting the capillary rise of water and resistance against salt crystallization.

Table 3. Compressive strength of the organic lime mortar.

Sl No.	Organic Lime Mortar/Specimens	(28D) N/mm^2	(56D) N/mm^2
1	Reference lime mortar	0.895	1.81
2	Kadukkai lime mortar	1.141	1.68
3	Cactus lime mortar	0.38	1.62
4	Hibiscus lime mortar	0.96	1.42
5	Aloe vera lime mortar	0.65	1.85
6	Jaggery lime mortar	1.91	2.76
7	Neelamari lime mortar	0.387	0.62
8	Kadukkai + p. jaggery	2.1	2.6
9	All mixed (organics)	0.839	1.55

3.2. TGA-DTA

The TG-DTA results for 28 and 56 days are shown in Figures 3 and 4. The decarbonation of $CaCO_3$ in all the mortars, reported in the range of 710–730 °C, was observed in the TG-DTA pattern. The weight loss for the reference lime mortar was between 25 and 27%, but the overall weight loss of the organics-added lime mortar resulted in higher mass losses, as shown in Table 4. The kadukkai lime mortar's total weight loss was reported in the range of 30 and 30.4% for 28 and 56 days. The TGA graph showing the endothermic peak at 138 °C with a weight loss of 4.49% represents the organic dehydration and at 418 °C, the dehydration of amorphous carbonates phases [13]. The decarbonation of calcite for KLM is reported at 719 °C, with mass losses of 13.85% and 17.55%, which are higher than the reference lime mortar on 28 and 56 days, as shown in Figures 3 and 4 and in Table 4. The cactus lime mortar showed two endothermic peaks at 445 °C and 712 °C with mass losses of 10.45 and 11.25% on 28th day, and the well-formed hydrated phases of the carbonates are represented with increased weight loss of 16.25% on 56th day, as compared to the reference lime mortar [4,13]. The hibiscus lime mortar (HLM) also showed similar endothermic weight loss peaks at 429 °C and 710 °C, with loss in the range of 7.93 and 9.83% at 28 days and an increased mass loss of 14.28% on the 56th day, which is lower than the reference lime mortar. The aloe vera lime mortar (ALM) reported the higher mass loss compared to all the experimental mortars in this study.

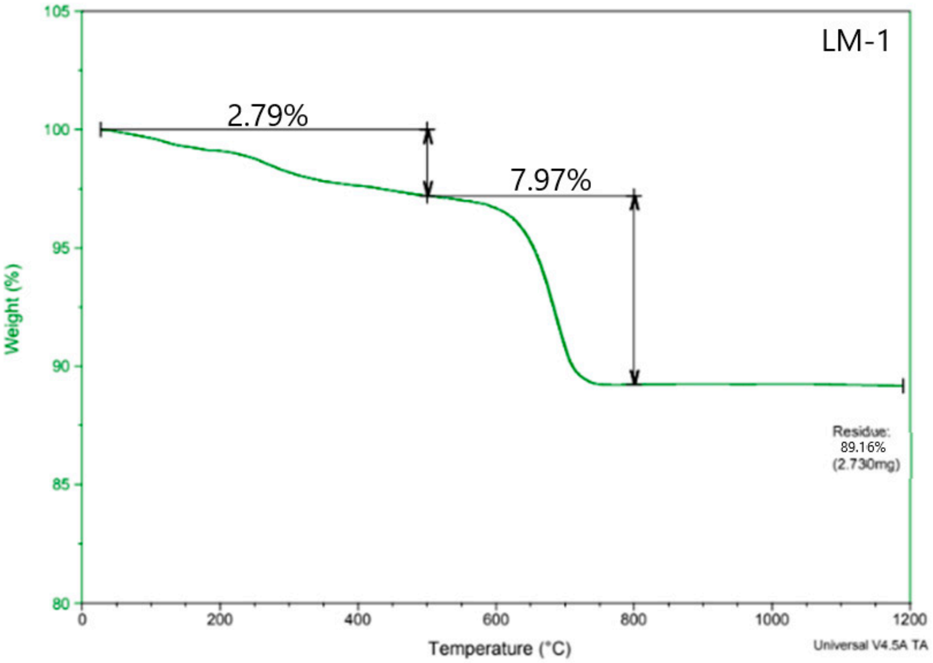

Figure 3. TGA-DTA pattern of the 28-days mortars: LM-1 Reference lime mortar (**a**) kadukkai; (**b**) cactus; (**c**) hibiscus; (**d**) aloe vera; (**e**) jaggery; (**f**) neelamari; (**g**) kadukkai + jaggery; and (**h**) kadukkai + jaggery + aloe vera (MXD).

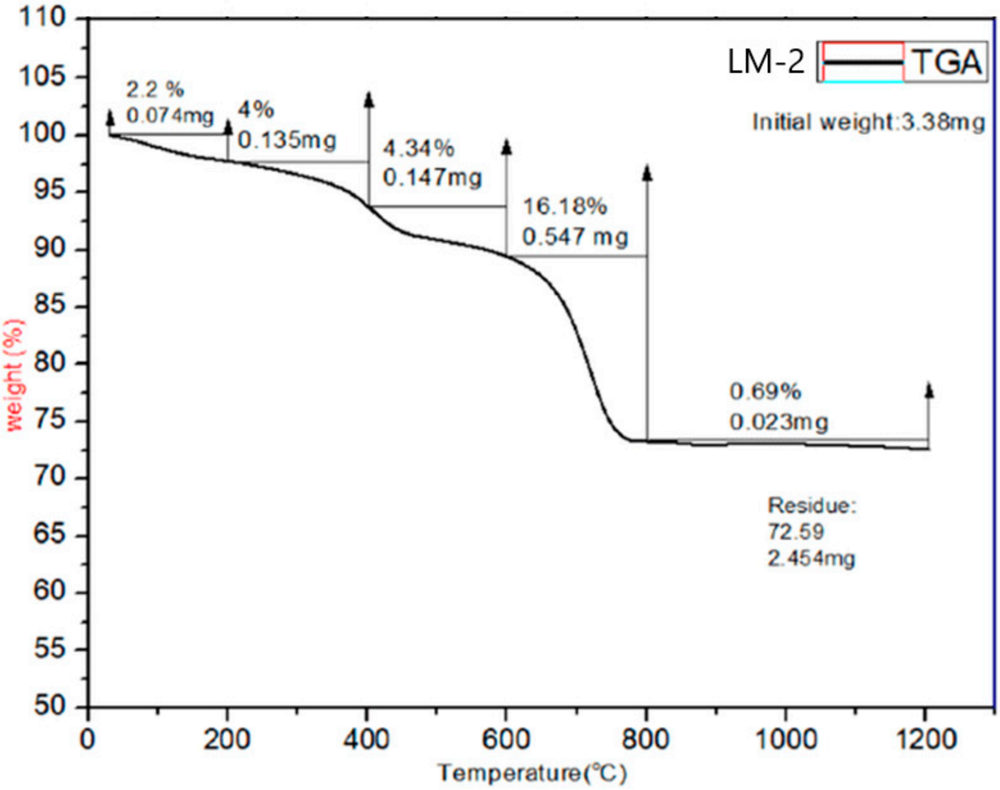

Figure 4. *Cont.*

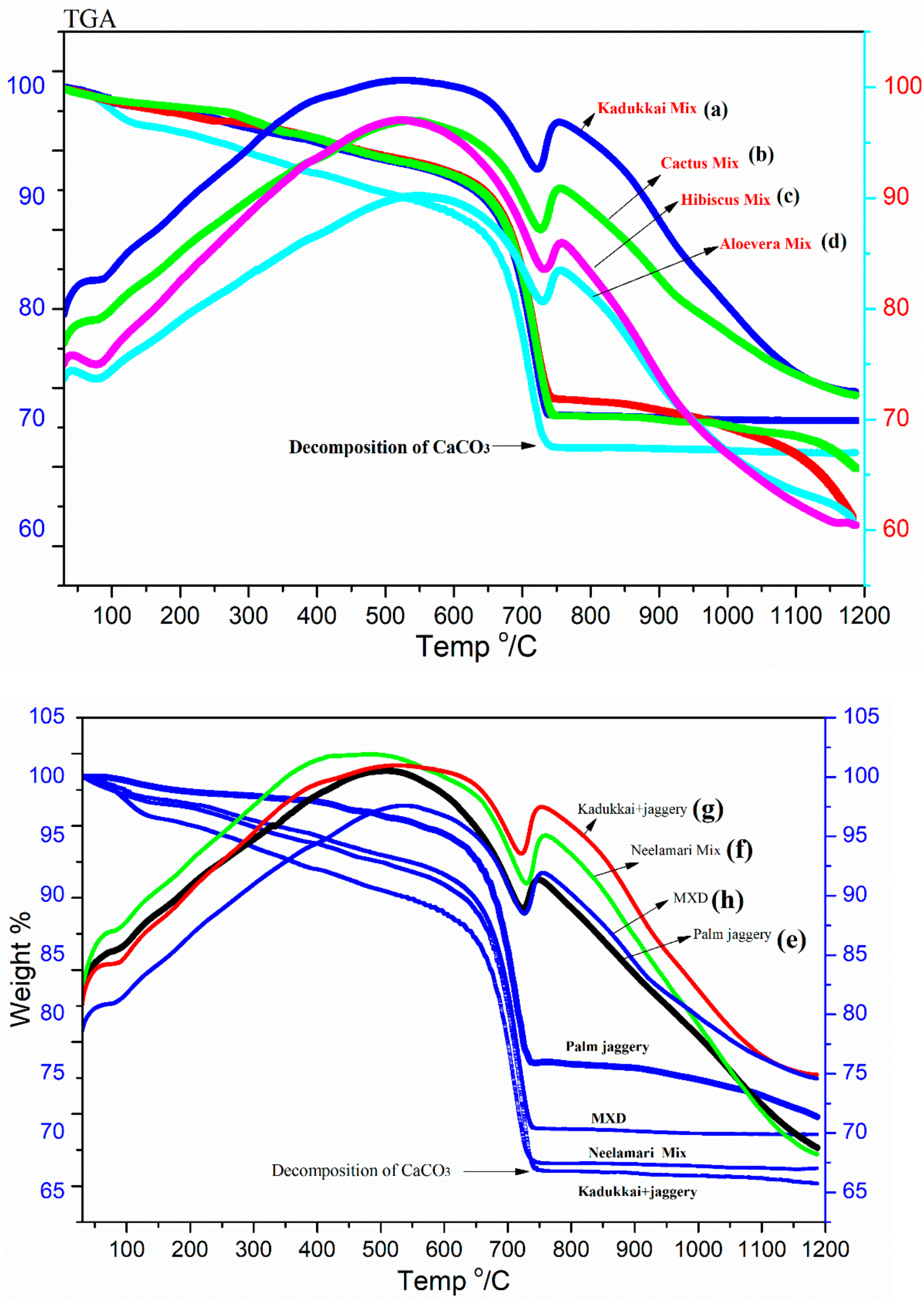

Figure 4. TG-DTA of 56-days mortars LM-2 Reference mortar: (**a**) kadukkai; (**b**) cactus; (**c**) hibiscus; (**d**) aloe vera; (**e**) jaggery; (**f**) neelamari; (**g**) kadukkai + jaggery; and (**h**) kadukkai + jaggery + aloe vera (MXD).

Table 4. TG-DTA weight loss of the lime mortar samples.

	Days	**Temperature–Weight Loss (%)**					
		0–200 °C	**200–400 °C**	**400–600 °C**	**600–800 °C**	**800–1000 °C**	**Total (%)**
Reference lime mortar	28/56 Days	2.42	5.51	7.51	9.76	0.65	25.85
		2.2	4	4.34	16.18	0.69	27.41
Kadukkai L.M		4.49	5.15	5.75	13.85	0.88	30.12
		4.1	4.3	3.56	17.55	0.89	30.4
Cactus L.M		2.72	4.85	10.45	11.25	1.51	30.78
		2.3	4.12	7.63	16.25	1.75	32.05
Hibiscus L.M		2.44	5.69	7.93	9.83	0.81	26.7
		2.1	4.22	4.25	14.28	0.89	25.74
Aloe vera L.M		2.72	4.85	14.21	12.03	1.51	35.32
		2.3	3.95	10.62	18.63	1.98	37.48
Jaggery L.M		2.62	4.95	7.52	11.25	0.67	27.01
		2.22	4.15	4.56	16.26	0.81	28
Neelamari L.M		2.54	3.76	7.13	16.5	0.78	30.71
		2.12	2.85	4.66	20.55	0.82	31
Kadukkai + P. Jaggery L.M		2.71	5.25	8.1	11.1	0.67	27.83
		1.98	4.65	5.6	15.45	0.85	28.53
All mixed (organics)		2.39	5.54	7.49	10.01	0.65	26.08
		2.2	4.1	4.44	16.18	0.69	27.61

The endothermic peaks at 447 °C and 723 °C with mass losses of 10.62 and 18.63% higher than all the other mortars confirm the higher calcite decarbonation. The jaggery lime mortar (JLM) reported a similar mass loss to the reference mortar, with 27 and 28%. The neelamari lime mortar (NLM) reported a mass loss of 20.55% on the 56th day, with a decarbonation peak observed at 745 °C, affirming the well-formed crystalline calcite formations on the addition of the fermented neelamari extracts. The rest of the mortars, such as KJLM and the all-mixed lime mortar (AMXD), reported similar mass loss ranges of between 27–28% compared to the reference lime mortar, but with higher decarbonation losses at 745 °C on the 15th day and 16% on the 56th day. The high mass loss was inferred for the aloe vera lime mortar, cactus lime mortar, jaggery mortar, and kadukkai + jaggery mortar on the basis of the decomposition of $CaCO_3$ on the 28th and 56th days. Compared to the reference mortar, high calcite precipitation is observed in the organically modified lime mortars. However, the high portlandite transformation to calcite is high in the organically modified lime mortar between 600–800 °C as compared to the low portlandite conversion between 400–600 °C for the reference mortar, as seen in Table 4. The supply of internal carbon dioxide from the organics quickens the hydration reaction, forming a higher-intensity calcite than that in the conventional mortar. The increased conversion of portlandite to calcium oxalates is supported by the XRD and FTIR data, and this is justified by the increased compressive strength of the organically modified lime mortars (Table 3) [25].

3.3. FT-IR

According to the FT-IR measurements in Figures 3–5, the organic mortars recorded calcite peaks of 1401, 869, and 711 cm^{-1}, silicate peaks of 1008 cm^{-1}, and portlandite (O-H) peaks of 3643 cm^{-1}, with broad hydroxyl group absorption peaks of 3341 cm^{-1}. A thin peak of aragonite and vaterite was detected at 1420 cm^{-1} and 856 cm^{-1} in jaggery, kadukkai

+ jaggery (KJ), and neelamari, indicating the early development of hydration products on the 28th day of curing. Improved initial binding due to the reaction of carbohydrates and fatty acids with portlandite was detected, which generated a network gel in the organic mortars [31]. KLM reported a wavelength peak at 869,1401 cm^{-1} as carbonates and 1008 cm^{-1} as a silica group, with an O-H peak at 3643 cm^{-1}. Similarly, all the organic added lime mortars reported similar wavelength peaks of calcite and silica groups, as shown in Figure 6. The TGA graphs showed percentages of mass losses at approximately 400–600 °C as the dihydroxylation of portlandite phases, which had shown similar peaks at 3643 cm^{-1}, as O-H peaks, in FT – IR of all the mortars, but there was no O-H peak in the reference lime mortar. The cactus lime mortar reported calcite peaks at 869 and 1404 cm^{-1} and an organic bend at 3341 cm^{-1}, along with a portlandite (O-H) peak at 3643 cm^{-1}. The presence of an organic bend was observed in the kadukkai lime mortar and the cactus mortar on 28th day. The kadukkai lime mortar had reported a higher spectral peak of calcite at 1409 cm^{-1} and an aragonite peak at 875 cm^{-1} on the 56th day. The jaggery lime mortar reported peaks of vaterite and aragonite at 871 and 875 cm^{-1}, respectively, indicating the addition of organics and the formation of carbonate polymorphs on the 56th day. According to the mineralogical phases of the XRD, the calcite, aragonite, and vaterite peaks were more profound on the 56th day compared to the 28th day, indicating well-developed carbonate polymorphs. In comparison, the organic mortar had a higher compressive strength than the reference lime mortar [4,13,31].

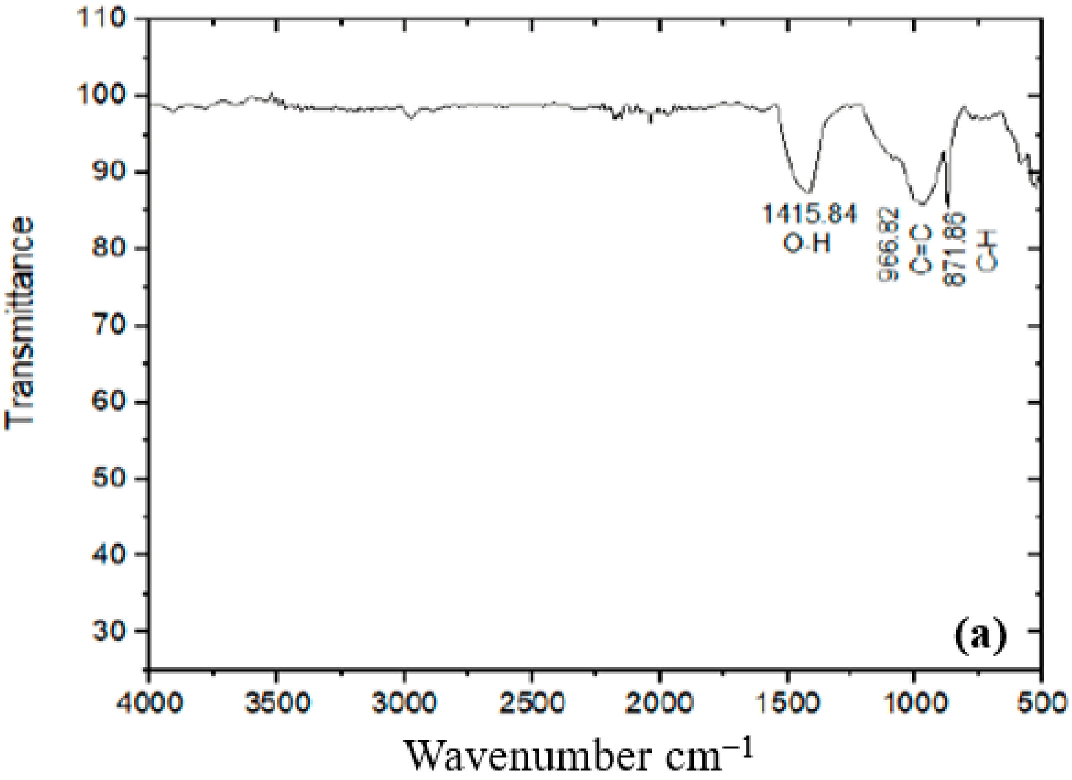

Figure 5. *Cont.*

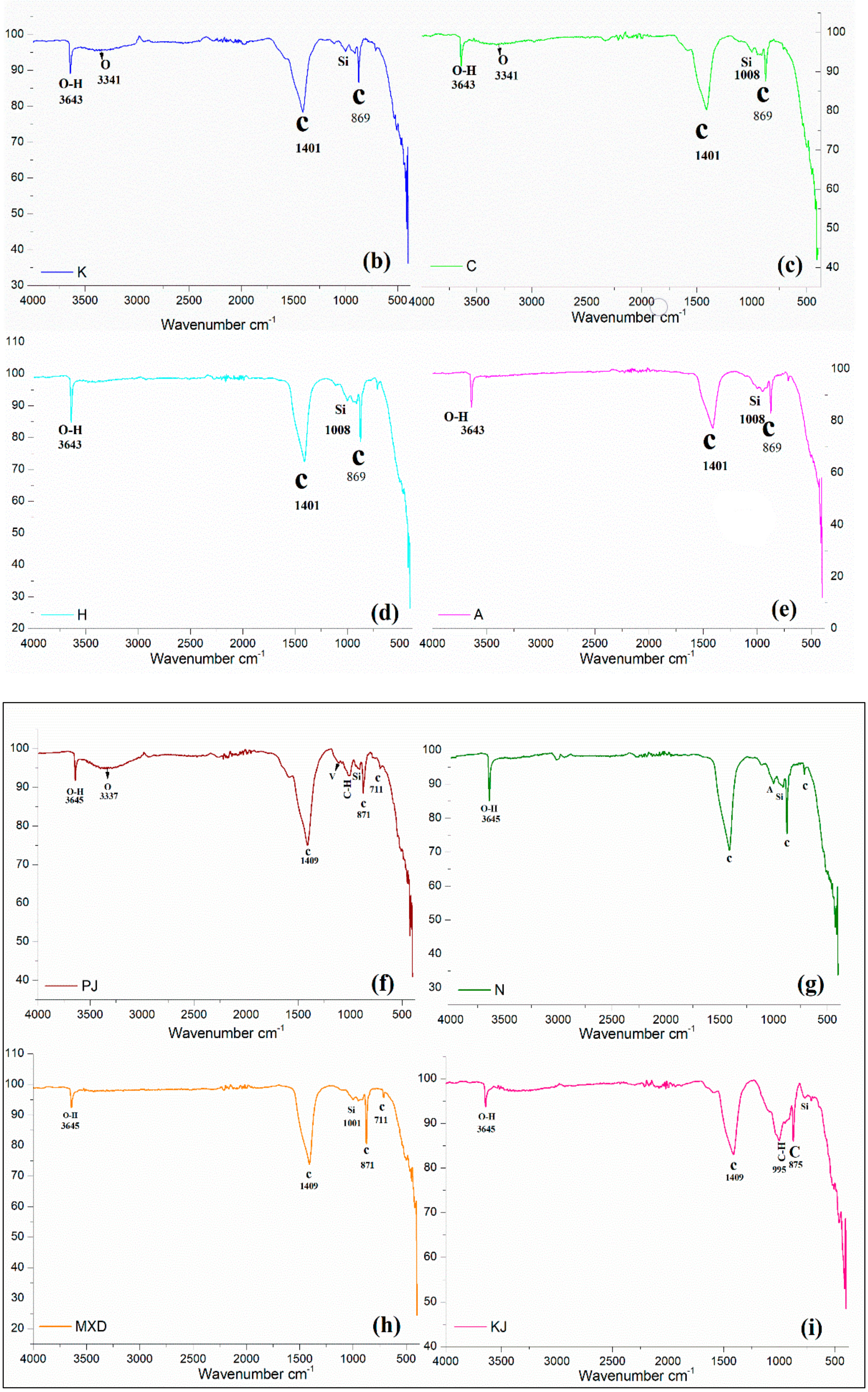

Figure 5. FT-IR patterns at 28 days: (**a**) reference lime mortar; (**b**) kadukkai lime mortar; (**c**) cactus lime mortar; (**d**) hibiscus lime mortar; (**e**) aloe vera lime mortar; (**f**) jaggery mortar; (**g**) neelamari lime mortar; (**h**) kadukkai + jaggery + aloe vera (MXD) mortar and (**i**) kadukkai + jaggery mortar; C: calcite, Si: silica, O-H: portlandite, O: organics.

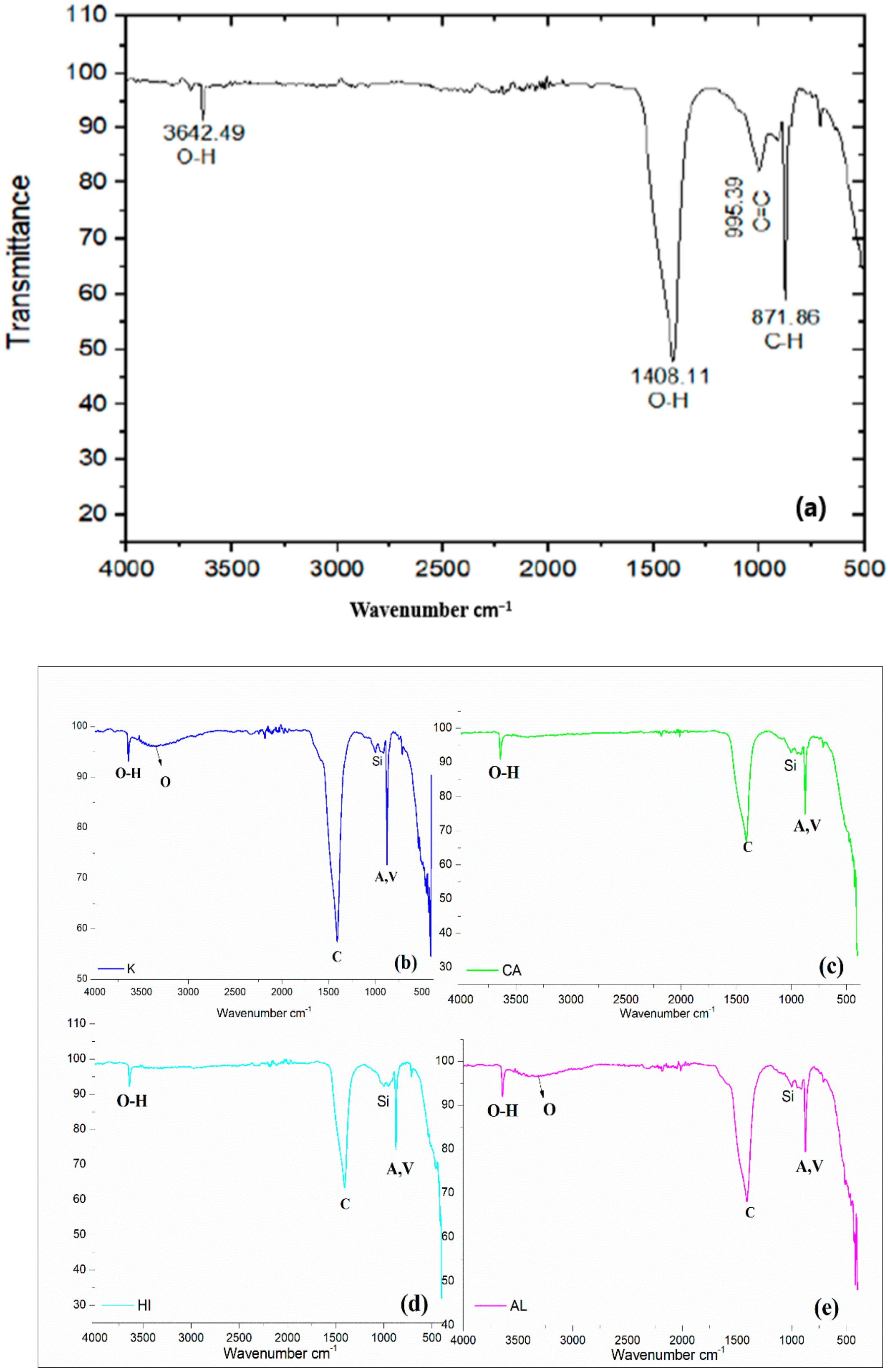

Figure 6. *Cont.*

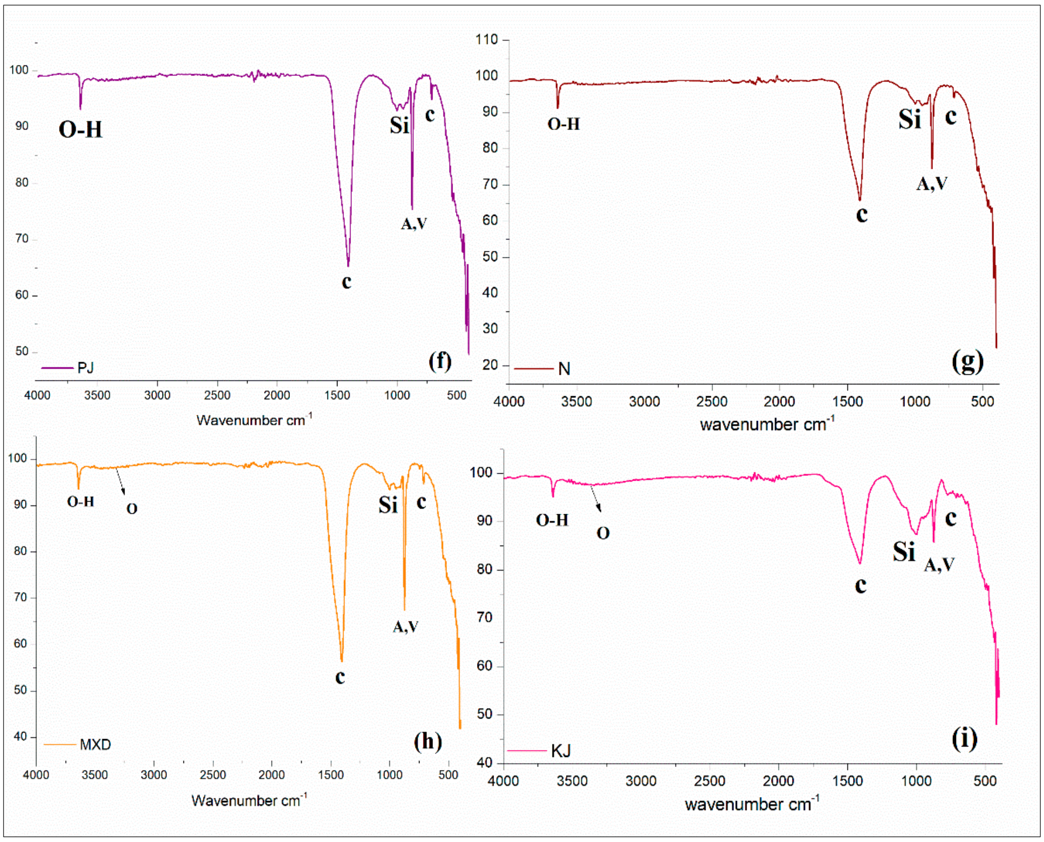

Figure 6. FTIR patterns at 56 days: (**a**) reference lime mortar; (**b**) kadukkai lime mortar; (**c**) cactus lime mortar; (**d**) hibiscus lime mortar; (**e**) aloe vera lime mortar; (**f**) jaggery mortar; (**g**) neelamari lime mortar; (**h**) kadukkai + jaggery mortar; and (**i**) kadukkai + jaggery + aloe vera (MXD) mortar. A: Aragonite, V: Vaterite, O: Organic peaks, Q: Quartz, C: Calcite.

3.4. Mineralogical Analysis

The XRD results of the reference lime mortar in Figures 7–9 represent the high-intensity calcite and portlandite peaks, along with quartz and minor traces of aragonite peaks. The existence of comparable oxides can be seen in the mineral peaks, which are well matched with the chemical composition. The XRD results for the aloe vera lime mortar (ALM), kadukkai + jaggery mortar (KJ), hibiscus mortar (HLM), cactus mortar (CLM), and kadukkai + jaggery + aloe vera lime mortar (KJALM) showed well-developed calcite peaks with reduced portlandite peaks (MXD) (Figure 8). As discussed earlier, the fermented extracts that were high in fatty acids, carbohydrates, polysaccharides, and other phytomolecules, as found in kadukkai, jaggery, hibiscus, and aloe vera, respectively, provide internal CO_2, which causes the lime mortar to carbonate and precipitate calcite in three different forms: aragonite, calcite, and vaterite crystals. The XRD studies suggest the formation of high-intensity portlandite peaks and calcium carbonate polymorphs during the early part of the curing time [26–31]. The rest of the organics-infused lime mortars, such as cactus, kadukkai, and neelamari, showed high portlandite peaks with calcite peaks on the 28th day.

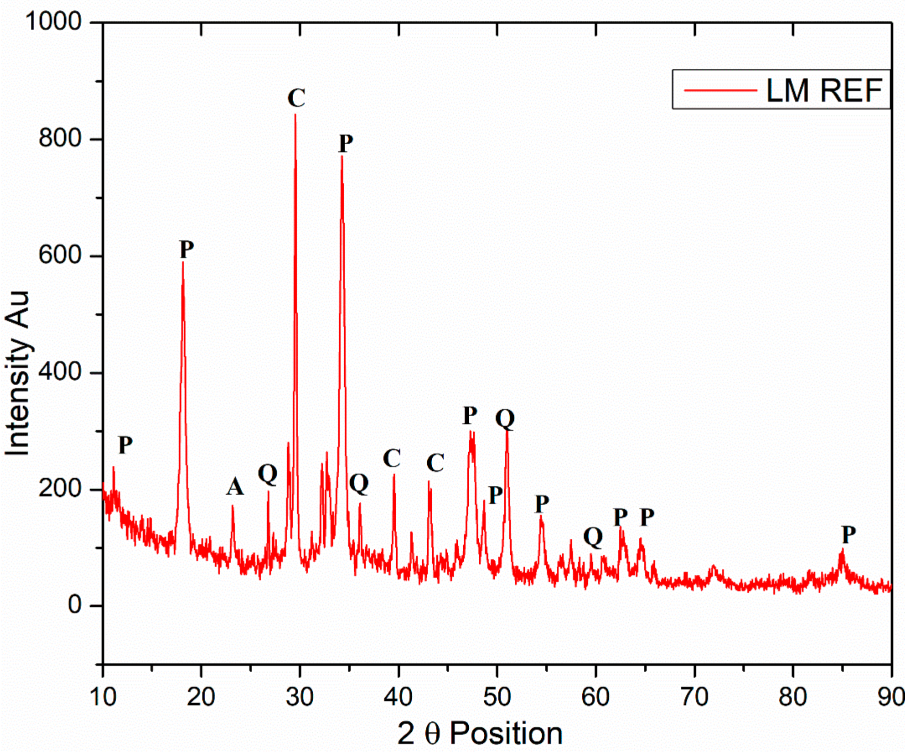

Figure 7. XRD patterns of the reference hydraulic lime mortar. P: portlandite, C: calcite, A: aragonite, T: tobermorite, Q: quartz, V: vaterite, W: Weddellite, G: gismondine-(CSH), AL: aluminium oxide.

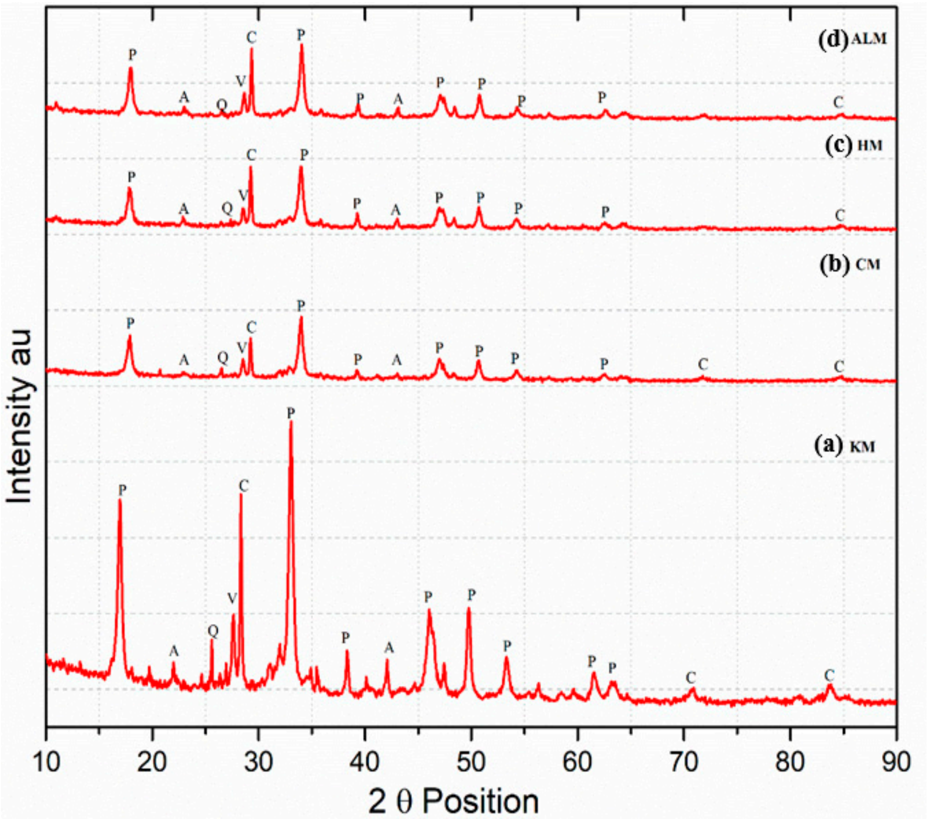

Figure 8. XRD patterns at 28 days: (**a**) kadukkai lime mortar; (**b**) cactus lime mortar; (**c**) hibiscus lime mortar; (**d**) aloe vera lime mortar. P: portlandite, C: calcite, A: aragonite, T: Tobermorite, Q: quartz, V: vaterite, G: gismondine-(CSH).

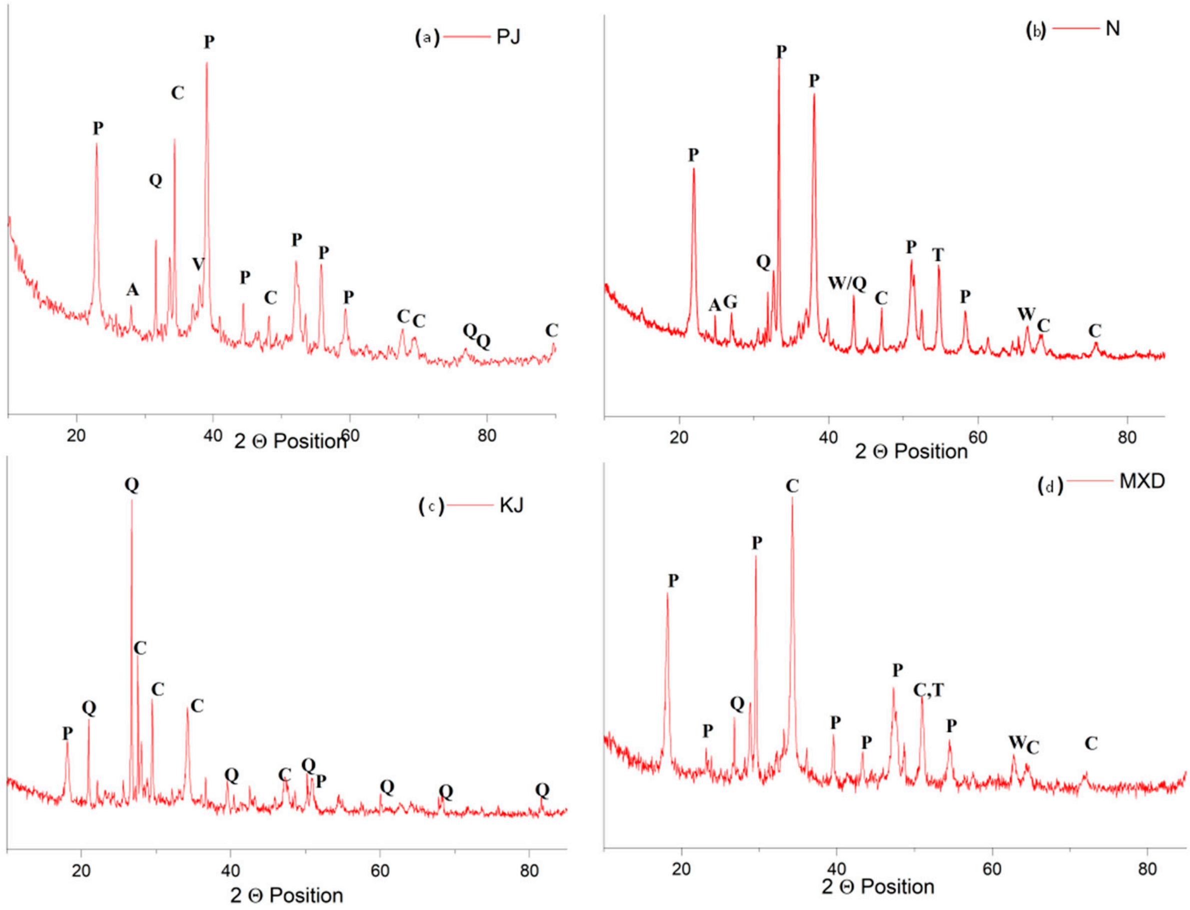

Figure 9. XRD patterns at 56 days (**a**) jaggery mortar; (**b**) neelamari lime mortar; (**c**) kadukkai + jaggery mortar; and (**d**) kadukkai + jaggery + aloe vera (MXD) mortar. P: portlandite, C: calcite, A: aragonite, T: Tobermorite, Q: quartz, V: vaterite, G: gismondine-(CSH), W: Weddellite.

The XRD results for the 56-day cured samples exhibited calcite polymorphs (calcite, aragonite, and vaterite) in all the organic lime mortars, including tobermorite and calcium oxalate (wollastonite), as the early production of the hydrated phases reported in the traditional organic mortars [28,29]. Figures 8 and 9 shows the highly developed calcite peaks compared to the reference lime mortar with organics, and it affirms the interaction between the formation of quick hydration products and the mechanical strength of the mortar. Mortar without organics has a higher amount of porosity, which increases the water-absorbing capacity of the mortar and lowers its resistance towards a compressive load. If more water molecules exist between two successive lime particles in the matrix, the binding strength is reduced, resulting in early failure. As a result, under compression, the mortar fails quickly [31]. The mineralogical formation of calcium oxalates is observed in the modified lime mortars due to the addition of fermented organics, which react with calcium oxide and form calcium alkoxides, which is not the case in the reference mortars. The mechanical strength of all the mortars, in comparison with the reference lime mortar, is reported in Table 3. Further, the interaction of the lime with the organics presents in the mortar led to the weight gain of the lime mortar due to the high rate of carbonation compared with reference mortar samples on the 28th and 56th days, respectively.

4. Conclusions

The addition of various fermented organics to lime mortar has been investigated and has shown increased carbonation depth and compressive strength. The presence of developed portlandite, gismondine, and minor calcium oxalates crystalline peaks observed in the cactus, kadukkai, and aloe vera mortars indicated the early formed hydrated phases compared to the reference lime mortar. The FT-IR results have substantiated the high-intensity calcite formation influenced by fatty acids, carbohydrates, and polysaccharides that had disintegrated into alcoholic components to interact with the portlandite crystals.

The carboxyl groups in fatty acids coordinate with calcium to form insoluble calcium salts of fatty acids; their non-polar units are directed to the mortar–air interface, resulting in a water-repellent property for the aloe vera and cactus lime mortars.

Water molecules cling to parts of hydrogen bonds in polysaccharide-rich organics such as hibiscus, aloe vera, and cactus, delaying the setting of time lime and moistening the mortar mix. Polysaccharides are more efficient in enhancing water retention and softening properties when they are pre-dissolved in mixing water. Because of the high surface tension between the pore water conveying CO_2 and the water-repellent matrix, the carbonation delay could be attributed to reduced CO_2 contact with calcium hydroxide in the reported liquid–solid interface.

The phytochemicals in all the lime mortars are responsible for a combination of chemical reactions such as water repellence, the retarding effect, and adhesive properties, which demonstrate the lime particle interaction that stops porosity, resists shrinkage cracks, and develops early mechanical strength with complete carbonation on the internal and external surfaces.

The TG-DTA results indicated the high-intensity calcite decarbonization observed in the kadukkai, jaggery, kadukkai + jaggery, and aloe vera mortars compared to the reference mortar. The highly carbonated mortars such as kadukkai, aloe vera, kadukkai + jaggery, and jaggery showed increased compressive strength due to the high-intensity calcite that formed in the presence of the fermented organics, releasing more CO_2 while reacting with the calcium oxide crystals.

The mortar samples rich in fatty acid (kadukkai) and polysaccharides (palm jaggery and kadukkai + jaggery) increased the compressive strength by 24 and 46% at 28 days and 65% at 56 days compared to the conventional mortar. This simulation study has produced a green recipe mortar to replace the traditional historic mortars of Padmanabhapuram Palace. The future scope of this research is to investigate the microstructure and pore sizes of each organics-added lime mortar and increase the curing periods beyond 56 days and up to 90,180, and 365 days, respectively.

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