CHAPTER 3
EXPERIMENTAL PROCEDURE

This chapter describes all the experimental procedures employed in this work to fabricate and characterize dental porcelains materials with their physical and mechanical properties tailored by method of ceramic nanocomposites approaches.

3.1 Sample Preparation

Preparation of dental porcelain powders and fabrication of ceramic nanocomposites have been employed as follow:

3.1.1 Powder Preparation

The as-received commercial dental porcelain powders are used as starting materials (Vita-VMK95, Vita Zahnfabrik, Bad Säckingen, Germany), which had particle size range of ~1.5-2.5 μm. Porcelain powders were mixed with 20 wt% of zirconia powders (Sigma-Aldrich, purity > 99%) by using a rapid vibro-milling for 30 min [3] (Micronisingmill McCrone Scientific Ltd., England) and left to dry for 6 hours at 120˚C in atmospheric furnace (Electrical furnace, Somsak supply, Thailand).

3.1.2 Preparation of the specimens

Green samples were obtained by mixing powders with polyvinyl alcohol binder (PVA) via a slip-casting technique as recommended by the manufacturer [142], and then poured into a standard stainless steel mould with a normal-sized cavity of 30 mm x 6 mm x 2 mm, reproducing the desired dimensions and shapes (Fig. 3.1 and 3.2) [2, 3]. After molding, the ceramics were fabricated by employing different firing schemes with heating rate of 25 ˚C/min in a vacuum furnace (Multimat Touch & Press, Germany) (Fig. 3.3), as detail demonstrated in Table 3.1. During heating, the temperature was maintained at 500˚C for 1 hour to burn out the PVA binder. The dental porcelain was sintered at 980˚C for 5 minutes as recommended by the manufacturer. Some samples of dental porcelain ceramics modified with 20 wt%

ZrO_2 additive, i.e. the control group (CG), were singly sintered at 1040˚C for 5 min [4]. Another group of samples (coded G1-G8) were sintered by employing the two-step sintering process and then quenched into room temperature. However, all of them were sintered in the same drying time (5 min), preheating time (5 min), heat rate (25˚C/min), and vacuum level at 0.05 atm. After firing, all specimens were serially ground and wet polished with 280, 400, 800 and 1,200 grade silicon carbide paper mounted on a metallographic lapping machine (Abramin, Struers A/S, Copenhagen, Denmark) to produce surface like a mirror. Finally, the specimens were cleaned using an ultrasonic bath with acetone at room temperature for 15 min (Fig. 3.4).

Table 3.1 The firing schemes employed for the production of samples.

Materials	**Firing condition**		
	Temp. /Dwell time (˚C/min)	**Temp./ Dwell time (˚C/min)**	**Quenched**
Dental porcelain	980/5	-	-
CG	1,040/5	-	-
G1	1,040/0	-	√
G2	1,040/1	-	√
G3	1,040/3	-	√
G4	1,040/5	-	√
G5	1,040/5	940/0	√
G6	1,040/5	940/30	√
G7	1,040/5	940/60	√
G8	1,040/5	940/90	√

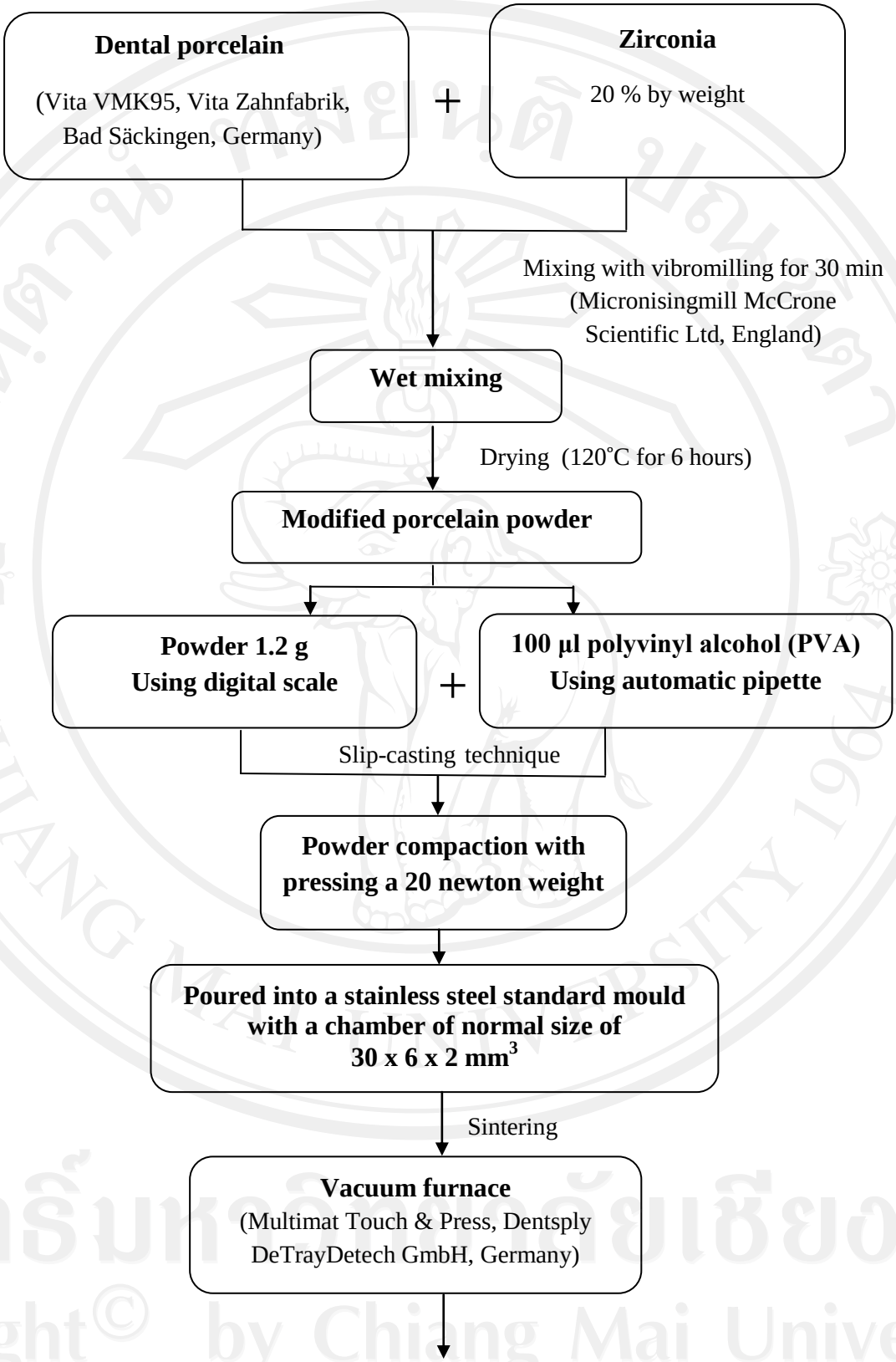

Fig. 3.1 Flow chart of green sample preparations.

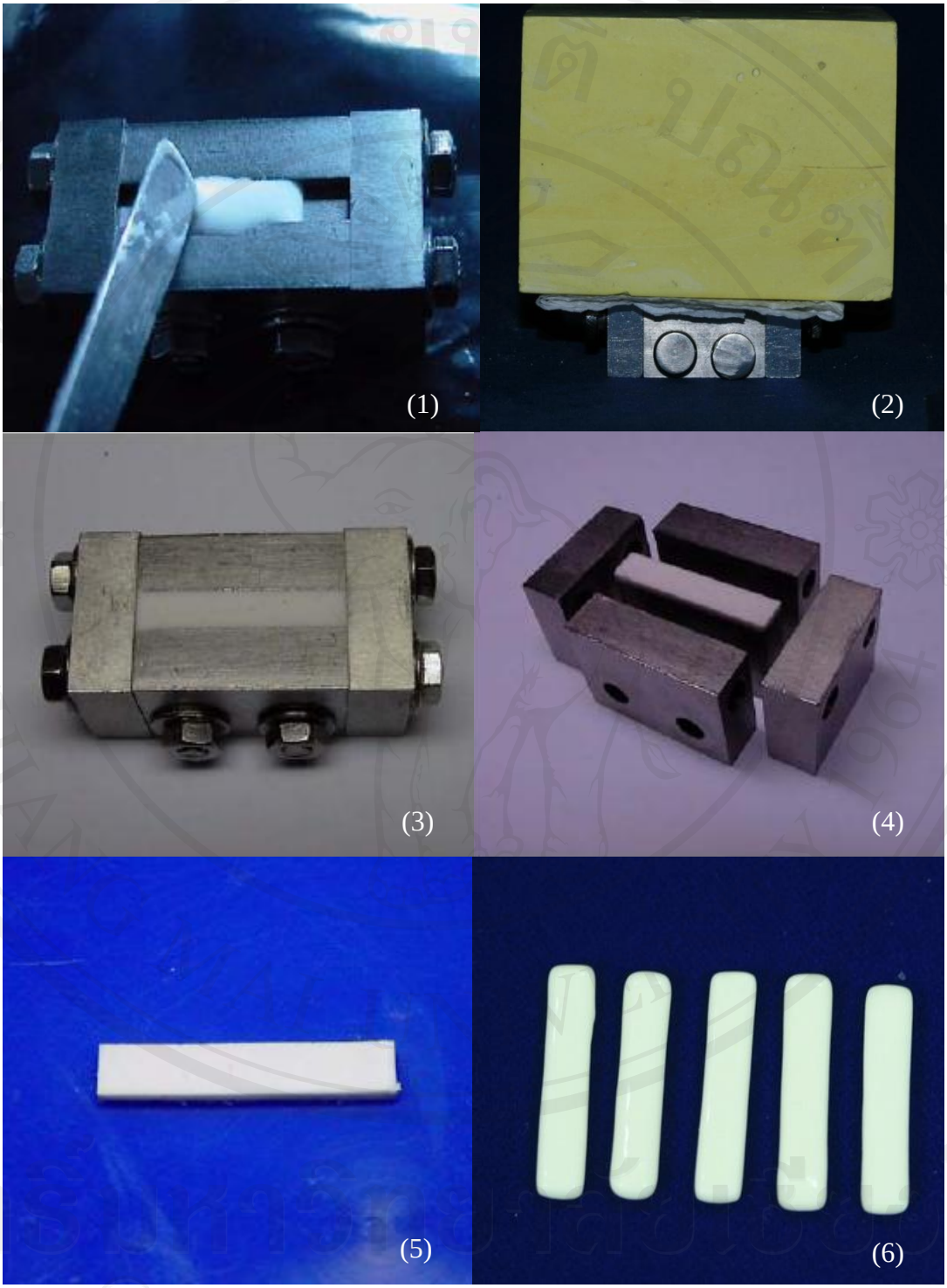

Fig. 3.2 Industrial shaping process of dental porcelain by slip casting technique: (1) pouring slip into the metal mold, (2) excess moisture removing, (3) surface flattening, (4) unpacking, (5) green specimen, and (6) sintered specimens.

Fig. 3.3 Vacuum furnace (for reducing sample porosity after sintering process).

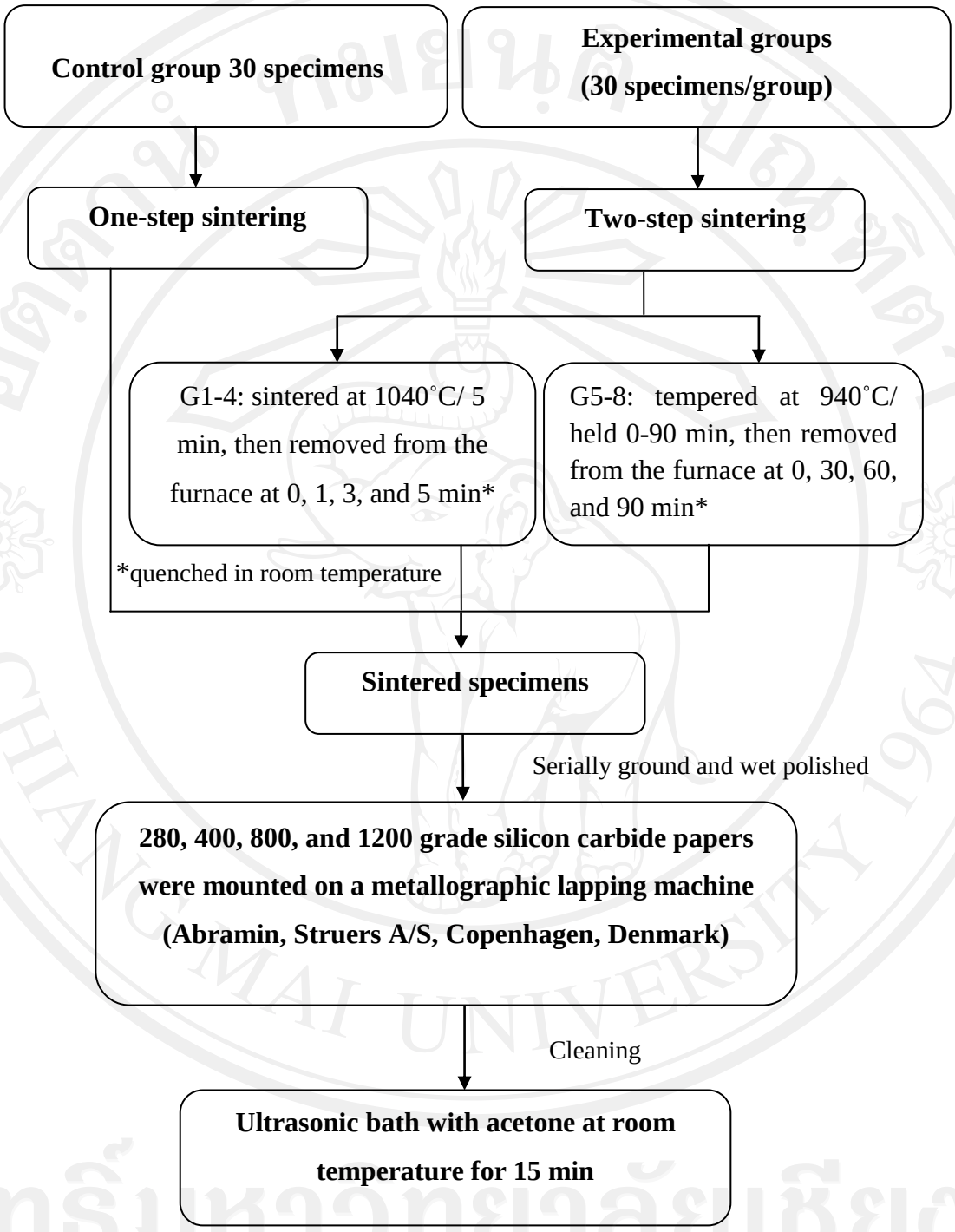

Fig. 3.4 Flow chart of the specimen preparations.

3.2 Sample Characterization

The following section is intended to address the main characterization techniques used to investigate the density, phase formation, content, size, morphology, and distribution of leucite in this study.

3.2.1 Density analysis

Densities of the final sintered products were determined by the Archimedes principle using xylene as immersion liquid at room temperature [143]. The density (ρ_c) was calculated according to the equation as follows:

$$\rho_c = \left(\frac{w_1}{w_2 - w_3}\right) \times \rho_{xylene} \quad \textbf{(3.1)}$$

where ρ_c and ρ_{xylene} is the density of ceramic and xylene in room temperature (ρ_{xylene} = 0.863 g/cm3). W_1, W_2 and W_3 is the dry weight of specimen, wet weight of specimen and weight of the specimen in xylene, measured using a digital scale (Fig3.5).

Fig. 3.5 Digital scale was used for measuring density by the Archimedes principle.

3.2.2 Phase analysis

X-ray diffraction (XRD) (X'pert MPD, Philips Corp, Japan) (Fig. 3.6) analyses were conducted to determine the crystalline phase formation and quantitative amount of the crystalline phase within the porcelain composite materials [83]. All samples were ground into powders, placed in the holder of a diffractometer and scanned with Cu Kα X-ray, 0.154056 nm λ at 40 kV and 45 mA.

3.2.3 Microstructural analysis

The 30 polished specimens per groups were section with carborundum disc in to specimen 2 x 2 x 2 mm in size. The specimens were etched with 2 vol% of hydrofluoric acid for 1 min, and platinum-coated (20 nm) for observe microstructure with low vacuum scanning electron imaging (SEM) (Philips XL 30, Philips Corp., Tokyo, Japan) and with a field emission SEM (JSM 6335 F, Jeol, Tokyo, Japan) (Fig. 3.7). The chemical composition of the phase formed was also elucidated by an energy dispersive X-ray (EDX) analyzer with an ultra-thin window. EDX spectra were quantified with the virtual standard peaks supplied with the Oxford Instruments eXL software.

3.2.4 Size analysis

The average crystallite size was determined using the diffraction peak (400) of the leucite pattern by using Scherrer equation [144]. Lattice parameters of the leucite phase were determined from the *d* spacings for the (400) and (004) peaks for the tetragonal phase [10, 11]. The grain size and morphologies of leucite phase in the sintered samples were determined from SEM micrographs. The mean crystallite size was calculated according to the equation as follows:

$$t = \frac{0.9\,\lambda}{B\cos\theta_B} \qquad \textbf{(3.2)}$$

where t is average crystallite size.

λ is the wavelength of the X-ray.

B is the full width at half maximum intensity of the peak.

θ_B is Bragg's diffraction angle.

Fig. 3.6 X-ray diffractometer.

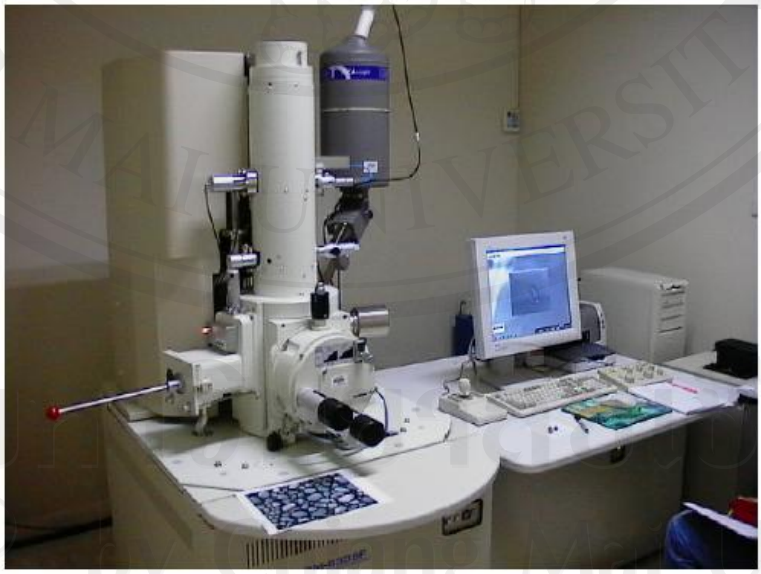

Fig. 3.7 Scanning electron microscope, equipped with EDX analyzer.

3.2.5 Mechanical properties measurements

3.2.5.1 Uniaxial flexural strength

The uniaxial flexural strength (*M*) was determined with the three-point bending test (Fig. 3.8) and calculated by the equation as follows [122]:

$$M = \frac{3Wl}{2bd^2} \quad \textbf{(3.3)}$$

where *W* is the breaking load (N), *l* is the test span (mm), *b* is the width of the specimen (mm) and *d* is the thickness of the specimen (mm). The specimens were tested with a universal testing machine (Instron® Universal Testing Machine, Instron 5560 Series, U.S.A.) (Fig. 3.9). Before testing the edges of the surface of the specimens undergoing tensile stresses were chamfered with a 9 μm grit size diamond disc.

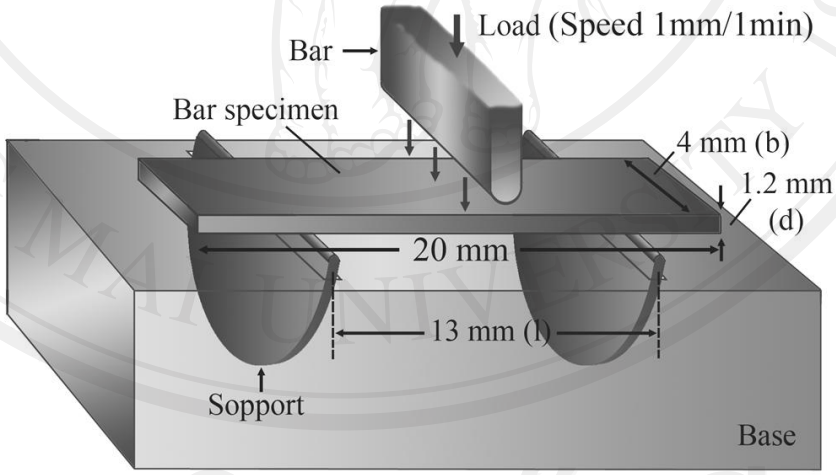

Fig. 3.8 Diagram of uniaxial flexural strength test shows rectangular-shaped specimen loaded from above by steel bar and supported from below by adjustable half-round steel plates.

Fig. 3.9 Universal testing machine.

3.2.5.2 Hardness and Elastic Modulus

Hardness (*H*) was determined and calculated by the Vickers microhardness testing machine (Galileo Microscan OD, UK) (Fig.3.10) with continuous depth recording method and indention load from 0.4-1 N in 20 steps of loading. The testing of both techniques were measured as recommended by the ASTM C 1259-01 [125] and C 1327-99 [126]. *H* can be calculated by the equation as follows:

$$H = (0.1020)(0.18544)\frac{P}{(d)^2} \quad \textbf{(3.4)}$$

where *P* is the load (N) and *d* is the average range of the two diagonals of the indentation (mm) (Fig. 3.11).

Young's modulus (*E*) was calculated by the rule of mixture (ROM) [145]. *E* can be calculated by the equation as follows:

$$E_c = V_{Dental}E_{Dental} + V_{Zirconia}E_{Zirconia} \quad \textbf{(3.5)}$$

$$V_{Dental} = v_{Dental}/(v_{Dental} + v_{Zirconia}) \quad \textbf{(3.6)}$$

$$V_{Zirconia} = v_{Zirconia}/(v_{Dental} + v_{Zirconia}) \quad \textbf{(3.7)}$$

where Ec is Elastic Modulus of ceramic composite (GPa).

E_{Dental} is Elastic Modulus of Dental ceramic.

$E_{Zirconia}$ is Elastic Modulus of Zirconia.

V_{Dental}, $V_{Zirconia}$ is volume ratio of dental ceramic and zirconia.

v_{Dental}, $v_{Zirconia}$ is volume of dental ceramic and zirconia (cm^3).

Fig. 3.10 Vickers microhardness testing machine.

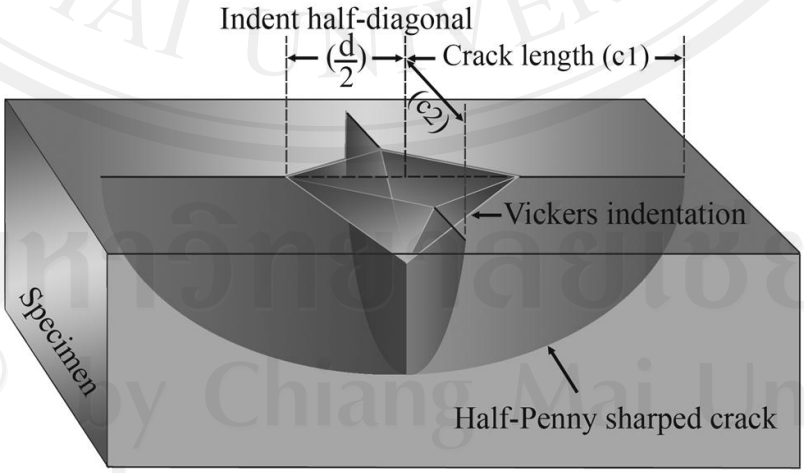

Fig. 3.11 Illustration of Vickers indentation and cracks formed around indentation. Dimensions of indentation and cracks to calculate indentation fracture toughness.

3.2.5.3 Indentation Fracture Toughness

Thirty specimens of each composition were polished with diamond paste (DP-suspension P, Struers A/S, Denmark) from 9 to 1 μm until a mirror-like surface was achieved and subsequently cleaned in an ultrasonic bath with acetone and dried at 120°C. The specimens were coated with a thin layer of platinum for making the light contrast of microhardness tests. This procedure is similar to hardness testing, but higher loads are used to create cracking around the indentation. The indentation technique was described by Anstis et al. [93, 146]. Loads of 20-60 N were applied to the specimens with a Vickers microhardness testing machine (Galileo Microscan OD, UK) (Fig. 3.8). Optimal testing loads for each material were determined by comparing the crack length from center of indentation with the length of the half-diagonal. A load must be used that produces a ratio greater than 2. It was determined that 30 and 50 N of load for 10 s should be used for the dental porcelain and the nine composite materials, respectively. Ten indentations were recorded for the length of the cracks at the four corners of each material under the microscope and the fracture toughness (K_{IC}) of the each material was calculated with the indentation strength method and also Young's modulus. The equation proposed by Fischer and Mark [147] as follows:

$$K_{IC} = \xi \left(\frac{E}{H}\right)^{1/2} \cdot \frac{P}{c^{3/2}} \qquad \textbf{(3.8)}$$

where ξ is a constant prefactor (0.018), E is the Young's modulus, H is the hardness, P is the indentation load and c is the crack length, calculated from the measured arithmetic means of c_1 and c_2 (Fig. 3.11).

3.3 Statistical Analysis

A multiple regression analysis was used to determine the significance of the influence of the surface and heat treatment on the flexural strength. Some physical property and strength data were analyzed by statistical technique of one-way ANOVA (with Scheffé's pairwise multiple comparisons were used to assess whether there was any statistical difference among groups and to identify which pairs of groups were

different) and Weibull analysis [148]. Statistical significant differences of the hardness, flexural strength and fracture toughness data between materials were analyzed with one-way ANOVA and Scheffé post hoc tests at a significance level (*p*) of 0.05 by SPSS ver. 14 program.

The Weibull moduli (*m*) were calculated for flexural strength data to characterize variability strength of all materials. Weibull parameters were estimated using the two-parameter Weibull distribution, and curve fitting was performed with a modified maximum likelihood estimator with mean reduced biasing adjustment. Ninety-five percent confidence bounds were placed on the estimates for the Weibull modulus and characteristic strength. A likelihood contour method was used for determining whether two Weibull distributions were statistically significantly different. This method is described in the New Weibull Handbook [149, 150]; however, simply stated, a horizontal slice is made in the three-dimensional contour plot of the Weibull distributions being compared at equal likelihoods. The plot has the 95% confidence bounds of the estimate for the Weibull shape parameter $\hat{m}$ on the Y-axis and the 95% confidence bounds for the estimate of the characteristic strength $\hat{\sigma}_\theta$ on the X-axis. It confidence bounds intersection, Weibull parameters are not statistically significantly different.

Weibull moduli are calculated by plotting *In In 1/(1-F*) versus *ln (s).* F is the median rank and can be calculated by the equation as follows [151]:

$$F = \frac{i-0.5}{n} \quad \textbf{(3.9)}$$

where *i* is the rank of a samples in terms of strength (*i* = 1 for the lowest strength sample), *n* is the total number of samples and *s* is the strength of sample *i*. A linear regression was done by the median rank regression method. The slope of the line is the Weibull modulus. Strength levels at 1, 5 and 10% probability of failure (P_f) were calculated using the Weibull plots by the equation as follows [6]:

$$P_f = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^m\right] \quad \textbf{(3.10)}$$

where σ is the strength at a given P_f and σ_0 is the Weibull characteristic strength, can be calculated by the equation as follows [6]:

$$\sigma_0 = \left(\frac{1}{n}\sum_{i=1}^{n} s^m\right)^{\frac{1}{m}} \quad \textbf{(3.11)}$$