Research Article

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Alternative of bone china and porcelain as ceramic hand molds for rubber latex glove films formation via dipping process

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Abstract: In general, the main compositions of porcelain and bone china composed of 54-65%wt silica (SiO_2), 23-34% wt alumina (Al_2O_3) and 0.2-0.7%wt calcium oxide (CaO) suitable for preparation high quality ceramic products such as soft-hard porcelain products for teeth and bones, bioceramics, IC substrate and magneto-opto-electroceramics. The quality of ceramic hand mold is depended on raw material and its properties (pH, ionic strength, solid-liquid surface tension, particle size distribution, specific surface area, porosity, density, microstructure, weight ratio between solid and water, drying time, and firing temperatures). The suitable firing conditions for porcelain and bone china hand-mold preparation were firing at 1270°C for 10 h which resulted in superior working molds for making latex films from natural and synthetic rubber. The obtained fired porcelain hand molds at 1270°C for 10 h provided good chemical durability (10%NaOH, 5%HCl and 10%wtNaCl), low thermal expansion coefficient ($5.8570 \times 10^{-6} (^\circ\text{C}^{-1})$), good compressive (179.40 MPa) and good flexural strength (86 MPa). While thermal expansion coefficient, compressive and flexural strength of obtained fired bone china hand molds are equal to $6.9230 \times 10^{-6} (^\circ\text{C}^{-1})$, 128.40 and 73.70 MPa, respectively, good acid-base-salt resistance, a smooth mold surface, and easy hand mold fabrication. Both obtained porcelain and bone china hand molds are a low production cost, making them suitable for natural and synthetic rubber latex glove formation.

Keywords: Eggshell coagulant, Slip casting process, Contact angle, Chemical durability, Thermal expansion coefficient

1 Introduction

Currently, green industries and environmental consciousness are gaining importance. Sustainable development and eco-efficiency are now main responsibilities in every country [1–4]. Most researchers pay attention to use of bio-materials, nontoxic materials, and recycled materials (biological wastes, bio-fibers and industrial wastes), and biodegradable materials as starting materials for research work [1–4]. Furthermore, the green products should have long lasting use.

Several materials are used to make casting molds including metal, glass, polymer, resin, silicone, rubber, wood, stoneware clay, porcelain, alumina, zirconia, and plaster. Some molds are temporary and are destroyed during the casting process [5], whereas more permanent molds are reused many times. The selection and design of materials for mold making are important depending on the final product requirements. Suitable molds for making natural rubber latex gloves depend on the glove required characteristics and properties such as film thickness, finished surface, elongation at break, optical clarity, tensile strength, and weight of films. Suitable molds must have the ability to induce a coagulation process of the rubber particles on the mold surface. Hand molds must be coated with various electrolytes to induce strong particle coagulation on the mold surface, to reduce the electrostatic repulsion between the latex particles and to induce high adhesion on the mold surface [6]. In general, porcelain, stoneware, plaster, bone china, and other ceramic molds have been known as casting molds for natural rubber latex (NRL) films. Ceramic hand molds have many advantages such as chemical resistance to electrolytes, good

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adhere to the mold surface and usually is dried prior to dipping the mold into the NRL compound [16–20]. The coagulant dipping time affects the thickness and smoothness of natural and synthetic rubber latex glove films [8–13, 16, 17, 20]. Eggs from hens, ducks and birds have been used as a source of food, drugs, cosmetics and foodstuffs. Eggshells are the egg product residue obtained from the production of eggs and egg derivatives and this waste contributes to environmental pollution as it supports microbial actions. The amount of eggshell waste from the food processing industry in Thailand has increased gradually up to millions of tonnes daily [16, 17, 19, 20]. As a by-product, eggshell represents about 11–15% of the total weight or approximately 60–75 g per egg and is composed of eggshell (including calcium carbonate (CaCO_3), magnesium carbonate (MgCO_3) and other oxide compounds) and eggshell membrane (including many kinds of fibrous proteins such as collagen, hexosamines, glycosaminoglycans, hyaluronic acid and sialic acid) [21]. From the previous study, adding eggshell acted as a flux with high amount 20 wt% yielded better physical-mechanical-thermal properties of the clay bio-bricks because the calcium oxide caused the calcium feldspar, calcium silicate and wollastonite phase formation [16, 17, 19]. The clay bio-brick can be sintered at low temperature 1000°C. Furthermore, the calcium oxide obtained from eggshell dissolved in 2M hydrochloric acid has an effect on the extracted amount of water soluble proteins in rubber latex glove film formation [17, 20].

The objective of the current study was to prepare ceramic hand molds made from porcelain and bone china via the slip casting process by varying the type of clay and firing temperature. The properties of the raw materials (porcelain and bone china clay) were characterized and measured, and the results are reported here. Furthermore, eggshell was used to prepare a liquid coagulant for preparation of natural and synthetic rubber latex glove films.

2 Experimental

2.1 Materials

Porcelain and bone china clays were supplied by Compound Clay Co., Ltd. Thailand. Potassium soap as the plaster mold releasing agent or liquid lubricant was supplied by Amarin Ceramics Corp., Ltd. Thailand. The potassium soap was composed of 87.05% wt potassium oleate ($\text{C}_{17}\text{H}_{33}\text{COOK}$), 1.69% wt fatty acid, and 11.26% wt alkaline solution or buffer solution with pH 10. The sodium

silicate solution used as a deflocculant was supplied by Amarin Ceramics Corp., Ltd. to adjust the viscosity of the clay slurry. The weight ratio between the clay slurry and sodium silicate was 100 kg: 250 g. Talcum or magnesium silicate powder ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) was used as the solid lubricant for casting the hand molds. Both Calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and calcium chloride (CaCl_2) as coagulant were prepared by using eggshell react to nitric acid and hydrochloric acid [16, 17, 20, 22], respectively, as shown in eq. (1) and eq. (2):

Eggshell is a good source of calcium that was easily obtained than other calcium sources. Eggshell waste is abundant in Thailand and other countries. The main composition of eggshell is calcium carbonate 96%wt and other 4%wt [16, 17]. It can react with nitric acid and hydrochloric acid to be calcium nitrate and calcium chloride, respectively, useful for function as coagulant. Coagulant adhered on the hand mold surface to form calcium-electrolytic coating layer. Calcium ions can help the latex particles adhere to form glove films on the hand mold surface [16, 17, 22]. Concentrated natural rubber latex (60%wt), additive, accelerator, antioxidant and vulcanizing agent were supplied by the Rubber Research Institute, Chatujak, Bangkok, Thailand. Nitro-synthetic rubber latex was supplied by Bangkok Synthetic Rubber, Rayong province, Thailand.

Instruments

An **X-ray fluorescence spectrometer** (XRF; Philips, model PW 2400) was used to determine the chemical compositions of raw materials with a tube current of 1000 mA and an acquisition lifetime of 30 s. An **X-ray diffractometer** (XRD; Bruker, D8 Discover) was used to collect data with subsequent analysis in a VANTEC-1 detector and a double-crystal wide-angle goniometer. Scans were obtained from 10° to 80° at 2θ and a scan speed of $2^\circ 2\theta/\text{min}$ in $0.02^\circ 2\theta$ increments using $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). Peak positions were compared with standard the Joint Committee Powder Diffraction Standards (JCPDS) files to identify the crystalline phases. **Fourier transform infrared spectroscopy** (FTIR; PerkinElmer, Spectrum One) was used at a spectral resolution of 4 cm^{-1} . The raw material and cured natural rubber film samples were measured to identify the chemical functional

groups in the range 400–4000 cm^{-1} . **Compressive and flexural strength** values of the fired porcelain and bone china hand mold samples were measured using a Universal Testing Machine (UTM; Hounsfield, H50KS) according to ASTM C165-95 [23] and ASTM D790-03 [24] with speed 10 mm/min. A **dilatometer** (Netzsch, DIL402PC; dimensions 5 mm $\times$ 5 mm $\times$ 25 mm) was used to measure the thermal expansion coefficient for fired clay hand mold. Thermal conductivity (Heat flow meter instrument, HC-074) was measured according to ASTM C518 [25]. The **viscosity or flow test** of ceramic slip was measured the proper amount of deflocculant by using viscometer (Brookfield Digital, DV-E). The **surface tension** of natural and synthetic rubber latex liquid suspension was measured using an automatic surface tensiometer (Kyowa, DY 300) with a DuNuoy Eing (platinum ring) or a Wilhelmy plate (platinum plate) at room temperature (25°C). The **contact angle** was used to measure the wettability and spreading of the liquid-solid interface using a contact angle meter (Kyowa, DM-CE 1). An **AUTOSORB-1** (Quantachrome; Florida, USA) was used to characterize the specific surface area, adsorption and/or desorption isotherms and pore size distribution. These material characteristics were evaluated by measuring the quantity of gas adsorbed onto or desorbed from the solid surface at equilibrium vapor pressure using the static volumetric method. The volume-pressure data were interpreted using the AUTOSORB-1 software to determine the Brunauer-Emmett-Teller (BET) surface area (single and/or multipoint), the Langmuir surface area, adsorption and/or desorption isotherms, micro-pore volume and surface area using an extensive set of built-in data reduction procedures. **Scanning Electron Microscope** (SEM, JEOL-5200) was taken and characterized the surface and cross-sectional area of ceramic hand molds fired at 1270°C and commercial hand molds. The samples were cut and mounted on a stub using carbon paste and were sputter-

coated to approximately 0.1 μm of gold to improve electrical conductivity with magnification of 20,000 time. **True density** of samples was measured according to the ASTM B212 [26] by a gas pycnometer (Quantachrome, Ultra pycnometer 1000) by boiling in hot water for 5 h, and cooling in water for 24 h, according to the ASTM C373 [27] in Eq. 3:

$$\rho = \frac{\text{weight } (D)}{\text{True volume}} \quad (3)$$

Where ρ is true density, D is the weight of sample after boiling and cooling, and true volume is the volume of solid component which all pores were destroyed.

Bulk density called apparent density is a property of granules, powders and others divided solids. Bulk density is not an intrinsic property of materials. It is defined as the mass of particles or samples divided by the total occupied volume. The total volume of bulk density includes particle volume, inter-particle void volume and internal pore volume. **Zeta potential** was measured by using a zeta potential analyzer (Malvern, Zetasizer Ver. 7.04) The zeta potential was used to measure the behavior of dispersion systems in liquid, latex and electrical double layer on solid/liquid interface. **Salt spray test** (SF/450/CCT/VH) was measured by immersion samples in NaCl solution $10 \pm 1\%$ wt at $50^\circ \pm 1^\circ\text{C}$ and pH 6.5–7.2. **Acid-base resistance** was measured by immersion samples in 5% HCl and 10% NaOH at 25°, 30°, 50°, 60°, 70° and 80°C for 18 h in each testing temperature.

2.2 Preparation of Ceramic Hand Molds

The weight ratio of porcelain or bone china clay: water: sodium silicate was 10 kg: 5 kg: 0.025 kg. All raw materials were mixed using agitation for 1 h to obtain a slip or slurry. The porcelain or bone china slip was poured into dried plaster hand molds. Furthermore, the porcelain and bone

Figure 2: Slip cast porcelain and bone china hand molds

china samples were cast in a rectangular shape (2.5 cm × 10 cm × 1.5 cm) and disc-like shape (diameter 3 inch) molds as solid products to prepare samples for property testing as shown in Figure 2a. Porcelain and bone china slips were prepared for the preparation of hand molds using the slip casting process resulting in a hollow product. After they had been casted from the plaster mold, they were allowed to dry at room temperature as shown in Figure 2b. The dried porcelain and bone china samples were fired at 1230°, 1260°, 1270°, 1280°, or 1300°C with a constant heating rate of 5°C/min in each firing for 10 h, as shown in Figures 2c and 2d. The weight and dimension of obtained ceramic hand molds after firing are approximately 450 ± 20 g, 7.0 cm of palm width × 34.5 cm of hand-former length, respectively. While the weight and dimension of commercial hand mold are 725 g, 9.5 cm of palm width × 38.5 cm of hand-former length. All fired clay samples were characterized for their physical (appearance, phase formation and microstructure), thermal (thermal conductivity and thermal expansion coefficient), and mechanical (compressive and flexural strengths) properties.

The optimum firing temperature of porcelain and bone china hand molds was selected from their characteristics on physical-mechanical-thermal properties and contact angle (wetting and spreading) of natural and synthetic rubber latex on hand mold surface by dipping process. Suitable sintering temperature called vitrification of ceramic hand mold was based on porcelain hand mold. Because the porcelain hand molds were compared physical-mechanical-thermal properties with those of commercial-porcelain hand mold for glove film formation by dipping in natural rubber latex. However, this current study, bone china hand molds were also studied physical-mechanical-thermal properties based on the obtained porcelain hand

mold. Therefore, both porcelain and bone china hand molds were fired and chosen at the same optimum sintering temperature. The best firing temperature of porcelain and bone china hand molds displayed a good result of rubber-latex film formation such as good film adhesion, short dipping time, smooth glove film, good film appearance and mechanical properties.

2.3 Natural Rubber and Synthetic Rubber Latex Compounds for Latex Glove Film Preparation

The formulas of the natural and synthetic rubber latex compounds were prepared according to Table 1. The latex glove film preparation was carried out using several steps. First the porcelain and bone china hand molds were cleaned and dried. Then, the hand molds were dipped into calcium chloride (CaCl₂) made from eggshell that functioned as the coagulant [16, 17, 19]. The main functions of a coagulant are to help in the pre-dip solution, to convert the liquid latex film to wet-gel on the mold, and to improve the release properties of the latex films from the molds [16, 17, 19, 22]. The coagulant dipping time was 3 s. This was followed by coating the hand molds with CaCl₂ and then dipping into the natural or synthetic rubber latex compounds for 15 s, after which they withdrawn slowly, and dried at room temperature. The coatings of NRL and synthetic rubber latex along with the porcelain and bone china hand molds, respectively, were cured in an oven at 120°C for 30 min, allowed to dry, and then detached from the porcelain and bone china hand molds as shown in Figure 3. They were subsequently characterized for their physical (thickness, film surface, colour and appearance), opti-

Table 1: Formulas of natural and synthetic rubber latex compounds for preparation glove films

Chemical substance	Weight (g)	Chemical substance	Weight (g)
60% natural rubber latex	167	Synthetic nitrile rubber latex	100
10% KOH, pH	2.00	3% KOH, pH	1.50
10% Terric 16A16	0.20	Sulfur, vulcanizing agent	1.10
50% Sulfur, vulcanizing agent	1.60	ZnO	1.30
50% ZDEC, secondary accelerator 'oizinc	0.80	ZDBC, secondary accelerator zinc diethyl	0.70
diethyl dithiocarbamate		dithiocarbamate	
50% Wingstay, antioxidant	2.00	TiO ₂ , additive	1.50
50%ZMBT, latex vulcanizing agent:	0.80	H ₂ O	150
Zinc-2-mercaptobenzthiazole			
50% TiO ₂ , additive	2.00		
50% ZnO	2.00		
H ₂ O	170.50

Figure 3: Rubber latex glove film preparation: a) dipping porcelain and bone china hand molds fired at 1270°C for 10 h coated with CaCl_2 prepared from eggshell into rubber latex compound; b) rubber latex glove film on hand mold surface after curing; c) removing glove film from hand mold; and d) final rubber latex glove films

cal (clearance and crack-free) and mechanical properties (tensile strength and elongation at break). A commercial ceramic hand mold was used as the reference mold, and glove samples were made using this mold according to the same procedures detailed above.

3 Results and Discussion

3.1 Physical and Chemical Properties of Ceramic Hand Molds

Physical properties *i.e.* true density, specific surface area, pore diameter and pore volume of raw materials (porcelain and bone china) and commercial hand mold were measured by a gas pycnometer and Ultra-quantachrome, respectively as data tabulated in Table 2. True density values of porcelain and bone china clay were measured according to ASTM B212 [27] equal to 2.40 and 2.58 g/cm³, respectively. While true density values of porcelain and bone china hand molds fired at 1270°C are 2.58 and 2.72 g/cm³,

respectively, close to that of commercial hand mold 2.53 g/cm³ and consistent with the results by Sokolar [28], Kitouni *et al.* [29] and Toludare *et al.* [30]. Both porcelain and bone china had high specific surface area equal to 13.52 and 10.96 m²/g, respectively. Bone china was very fine particle due to the lowest pore diameter and pore volume equal to 125.60 Å and 0.0349 cm³/g, respectively.

The comparison of chemical composition among porcelain and bone china clay, and commercial hand mold was measured by using XRF as shown in Table 3. The chemical components of the porcelain were 64.70%wt SiO₂, 22.60%wt Al₂O₃, and 12.70%wt other oxide, while the bone china consisted of 51.74%wt SiO₂, 41.99%wt Al₂O₃, and 6.27%wt other oxide compounds. The different metal oxides (K₂O, Na₂O and CaO) affect to feldspar formulas as a flux or sintered aid namely potash-feldspar (K), sodium-feldspar (Na) and calcium-feldspar (Ca), respectively. Total amount of feldspar in porcelain, bone china and commercial hand mold were 4.33%, 4.05% and 6.81%wt, respectively effect to decrease firing temperature of clay products. However, amount of alumina content was an important chemical component in the raw material of hand molds

Table 2: Physical properties of raw materials and commercial hand mold

Raw materials	True density (g/cm ³)	Specific surface area (m ² /g)	Pore diameter (Å)	Pore volume (cm ³ /g)
Porcelain clay	2.40	13.52	460.30	15.5600
Bone china clay	2.58	10.96	125.60	0.0340
Commercial hand mold powder	2.53	0.06	1418.00	0.0021
Porcelain hand mold fired at 1230°C	2.45	-	-	-
Porcelain hand mold fired at 1270°C	2.58	-	-	-
Bone china hand mold Fired at 1230°C	2.69	-	-	-
Bone china hand mold Fired at 1270°C	2.72	-	-	-

Remark: “-” means not measured.

Table 3: Comparison of chemical composition between porcelain and bone china clays using XRF

Chemical composition	Porcelain clay for hand mold preparation (% wt)	Bone china or vitreous china clay for hand mold preparation (% wt)	Commercial hand mold (% wt)
SiO ₂	64.70	51.74	63.74
Al ₂ O ₃	22.60	41.99	25.60
Fe ₂ O ₃	0.41	0.24	1.34
MgO	0.08	0.62	0.27
CaO	0.22	0.65	1.48
Na ₂ O	1.26	1.66	1.69
K ₂ O	2.85	1.74	3.64
TiO ₂	0.06	0.02	0.43
P ₂ O ₅	-	0.13	-
Loss of ignition	7.82	1.21	1.81
Total	100.00	100.00	100.00

Table 4: Mean viscosity ($\pm$ SD) of clay slip

Sample	Slip viscosity (cP)
Porcelain slip, 30 rpm, 80-100%	1043.83 $\pm$ 10.89
Bone china slip, 100 rpm, 80-100%	318.20 $\pm$ 10.64

because it had a high melting temperature to increase the physical, thermal and mechanical properties of hand molds providing good thermal shock resistance, low thermal expansion coefficient and high strength. Especially bone china contained alumina more than porcelain and commercial hand molds approximately 16.39-19.39%wt.

Table 4 shows the viscosity values of the porcelain and bone china clay slips measured using a viscometer. The viscosity values of slip casting depended on the electrophoretic charges, diluent, thixotropic degree, organic and coagulant as dispersion medium effect to porosity and quality of ceramic hand molds. Viscosity leads to a thick layer or body of densely packed particles along the mold walls. To manufacture desirable and reproducible ceramic hand molds with slip casting, numerous parameters such as particles size of the porcelain and bone china clay, viscosity, mold type, casting time and temperature, pH, and additive organic polymer properties need to be carefully controlled [31–33]. The effect of adding sodium silicate enhanced the casting performance of porcelain and bone china slip. Sodium silicate increased electric conductance, dynamic flow, rheological phenomena, Stern potential, zeta potential to forming and casting, and thickness of double layer around the particle. The porcelain (high Si⁴⁺ content) had a viscosity value higher than the bone china (high Al³⁺ content) as the data reported in Table 3 due to the electrical charging. The bond length values of

Si-O and Al-O were equal to 1.712 and 1.581 Å, respectively, supported the local charge balance, stability, physical and chemical properties. The positive electric charges (i.e. Al³⁺, Si⁴⁺, K⁺, Na⁺, Ca²⁺ and Ti⁴⁺) on the edge of clay particles were attracted to the negatively charged surfaces (sodium silicate as a dispersion medium) or coagulant (CaCl₂ or Cl⁻) on the hand mold surface. Charge density values of Al³⁺, Si⁴⁺, Ca²⁺, Na⁺, Ti⁴⁺, K⁺ were 364, 970, 52, 24, 362 and 11 (C.mm⁻³), respectively. When silicate ion (SiO₃)⁻² as the active ions was added and adsorbed to the clay particle surface, it can increase the viscosity and zeta potential because of the direct action at the surface charges as shown in Figure 4. Therefore, commercial hand mold, porcelain slip and porcelain hand mold fired at 1270°C had the zeta potential values higher than that of bone china slip and bone china hand mold fired at 1270°C. However, bone china hand mold fired at 1270°C was the most suitable for natural rubber latex because the zeta potential values of bone china hand mold was close to natural rubber latex at pH 10.5 to form solid gel or latex film casting. The obtained zeta potential was in the range $\pm$ 40 to $\pm$ 60 mV meaning of good stability whereas the zeta potential was higher than $\pm$ 60 mV meaning excellent stability [2, 34–36]. In addition, the bone china contained alumina content (41.99%wt) higher than that of porcelain (22.60%wt). Alumina is a non-plastic material with a high melting temperature up to 2072°C. Alumina help to increase thermal resistant properties. Furthermore, the viscosity values are important for determining the setting time, draining time for the plaster molds, and the thickness and weight of hand molds after casting. In addition, Sokolar [28], Kitouni *et al.* [29] and Toludare [30] reported using fluxing agents (sintered aids) and binders affected to sintering tempera-

Initial pH of NRL was 5.89. Concentrated NRL or pure latex initial pH was 5.89 before adjusting the pH versus zeta potential. The NRL compound was used to make the latex gloves with the pH of 10.5. The CaCl_2 acted as a coagulant for NRL glove film formation with the pH of 2-3. Colloids with high negative or positive zeta potentials are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate as follow (zeta potential (mV): stability behavior of the colloid) [15–17]:

1. If the zeta potential value is in the range 0 to ± 5 mV, it means rapid coagulation, precipitation, or flocculation.
2. If the zeta potential value is in the range ± 10 to ± 30 mV, it means incipient instability and beginning to agglomerate.
3. If the zeta potential value is in the range ± 30 to ± 40 mV, it means moderate stability.
4. If the zeta potential value is in the range ± 40 to ± 60 mV, it means good stability.
5. If the zeta potential value is more than ± 61 mV, it means excellent stability.

Figure 4: Comparison of zeta potential natural rubber latex on commercial, porcelain and bone china hand molds after firing at 1270°C

ture, microstructure and physical-mechanical properties of porcelain and bone china.

The FTIR spectra of clay, fired clay hand molds, and commercial hand mold are shown in Figure 5 consistent with the FTIR results reported by Beketova, *et al.* [37], Lenza, *et al.* [38] and Aguiar, *et al.* [39]. The ν (Al-O) and ν (Al-O-Si) were wave numbers 431, 460-471, 648, and 694 cm^{-1} . The ν (Si-O-Si) and $(\text{PO}_4)^{3-}$ of the FTIR spectra were at wave numbers 537-555, 913, and 938 cm^{-1} , respectively. In addition, wave numbers 779 and 794 cm^{-1} belonged to ν (Ca-O), ν (Ca-O-Si), ν (Al-O-Si), and ν (Si-O). The chemical functional groups of $\nu(\text{C}=\text{O})$ and CH_3 of $(\text{CO}_3)^{2-}$ asymmetric deformation were at 1419 and 1625 cm^{-1} , respectively, while $\nu(\text{OH})$ was at 3437-3444 and 3695 cm^{-1} . Furthermore, a double peak at 574 and 600 cm^{-1} was assigned to phos-

Figure 5: FTIR spectra of raw clay powder, fired porcelain and bone china clay hand molds, and commercial ceramic hand molds

Figure 6: XRD peak patterns of porcelain and bone china hand molds before and after firing at 1270°C (M-mullite, Q- SiO_2 -quartz, T-calcium phosphate, C- Al_2O_3 -alumina-corundum, N-sodium aluminosilicate hydrate)

phate group $\delta(\text{PO}_4)^{3-}$ and indicated the crystallization of Ca-P phase of bone china.

The XRD peak patterns of the raw materials and of the dried and fired molds are shown in Figure 6 consistent with the results reported by Sokolář, *et al.* [40] and Beketova, [37]. The XRD peak patterns of the porcelain clay had the five highest peak positions at 2θ equal to 6.1894° (100%), 23.7103° (49.5%), 15.7047° (36.9%), 20.9197° (36.4%), and 27.1183° (28.4%) consistent with

the JCPDS nos. 00-043-0168 of sodium aluminium silicate hydrate ($\text{Na}_2\text{Al}_2\text{Si}_4.5\text{O}_{13} \cdot x\text{H}_2\text{O}$) in cubic phase formation. The XRD peak patterns of the bone china clay had the five highest peaks at 26.6294° (100%), 12.3279° (34.5%), 35.1300° (28.6%), 24.8616° (25.20%), and 20.8626° (23.20%) consistent with the JCPDS nos. 00-051-0200 of calcium phosphate ($\text{CaH}_2\text{P}_2\text{O}_7$) in monoclinic phase formation, 01-070-0359 of monetite (CaHPO_4) in triclinic phase formation, and 01-070-1381 of calcium hydrogen phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) in triclinic phase forma-

tion consistent with the results reported by Sokolář [40]. The XRD peak patterns of the commercial ceramic hand mold had the five highest peak position at 26.6379° (100%), 26.3412° (49.5%), 26.0655° (36.9%), 20.8538° (36.4%), and 16.5028° (28.4%) consistent with the JCPDS nos. 00-046-1045 (SiO_2) of hexagonal phase formation and 00-010-0394 (mullite, $\text{Al}_6\text{Si}_2\text{O}_{13}$) of orthorhombic phase formation consistent with the results reported by Sokolář *et al.* [40] and Beketova *et al.* [37]. The XRD peak pattern of the fired porcelain hand mold was consistent with the XRD

Figure 7: SEM micrographs of ceramic hand molds at surface and cross-sectional area with a magnification of 20,000X: a) and a-1) commercial hand molds; b) and b-1) porcelain hand molds fired at 1270°C , c) and c-1) bone china hand molds fired at 1270°C

Table 5: Salt spray, acid-base resistance, crazing and the percentage of weight loss of porcelain and bone china ceramic hand molds

Sample	Salt spray	Acid-base	Crazing	Weight loss (%)
Porcelain hand mold fired at 1230°C	x	✓	x	1.2266
Porcelain hand mold fired at 1270°C	x	x	x	0.3870
Bone china hand mold fired at 1230°C	x	x	x	0.1494
Bone china hand mold fired at 1270°C	x	x	x	0.0686
Commercial ceramic hand mold	x	x	x	0.5869

Remark:

Sign “x” means no crack and no any effect on ceramic hand mold surface.

“✓” means damaging from acid-base testing.

results of the commercial ceramic hand mold at the same peak position.

The salt spray testing, acid-base resistance, crazing and the percentage of weight loss of porcelain and bone china ceramic hand molds were data tabulated in Table 5. Porcelain and bone china hand molds fired at 1270°C and commercial hand molds were good to resist the chemical reagents *i.e.* salt solution, strong acid and base solvent. Furthermore, the SEM micrographs of obtained porcelain and bone china hand molds after firing at 1270°C were dense, small pore diameter and low pore volume especially bone china hand mold as shown in Figures 7c and 7c-1.

3.2 Mechanical and Thermal Properties of Ceramic Hand Molds

The mechanical and thermal properties of the ceramic hand molds are shown in Tables 6 and 7, respectively. The porcelain hand mold fired at 1270°C had the highest compressive strength and flexural strength equal to 179.4 MPa and 86.0 MPa, respectively, which were better than for the bone china hand molds. The chemical composition of the porcelain was 64.70%wt SiO₂ while the bone china had only 51.74%wt SiO₂ measured by using XRF. In addition, the bone china hand molds fired at 1270°C had thermal conductivity lower than the porcelain hand molds due to

the high alumina content (41.99%wt) as data tabulated in Table 3. However, all hand molds (porcelain, bone china and commercial ceramic hand molds) had thermal conductivity values close to natural and synthetic rubber in the range 0.13-0.25 W/m·K, respectively, as reported by Callister [14] and Çengel [15] making them suitable for latex glove preparation using the dipping process. The same thermal conductivity values between hand mold and latex films during the dipping process resulted in good wetting and spreading of the latex glove films coated on the fired clay hand mold surface. The commercial, porcelain and bone china ceramic hand molds fired at 1270°C had thermal expansion coefficient values of 5.8494×10^{-6} , 5.8570×10^{-6} and 6.9230×10^{-6} (°C⁻¹), respectively, consistent with the theoretical thermal expansion coefficient of porcelain and bone china reported by Callister [14]. The standard thermal expansion coefficient values of Al₂O₃, SiO₂, bone china and porcelain are 7.6×10^{-6} , 0.4×10^{-6} , $(6.5-7.2) \times 10^{-6}$ and $(7.0-14.0) \times 10^{-6}$ (°C⁻¹), respectively, reported by Callister [14]. In addition, the standard heat capacity values of Al₂O₃, SiO₂, porcelain and bone china are 775, 740, 1070-1085 and 850 J/Kg·K, respectively, reported by Callister [14].

Table 6: Comparison of mechanical properties of porcelain, bone china and commercial ceramic hand mold samples

Samples	Maximum load (N)	Compressive strength (MPa)	Flexural strength (MPa)
Porcelain hand mold fired at 1230°C	4615.00	96.60	91.10
Porcelain hand mold fired at 1270°C	8510.00	179.40	86.00
Bone china hand mold fired at 1230°C	3604.00	80.30	46.50
Bone china hand mold fired at 1270°C	6067.50	128.40	73.70
Commercial ceramic hand mold	4903.25	129.60	89.20

Table 7: Thermal expansion coefficient values of porcelain, bone china and commercial ceramic hand mold samples

Sample	Sample thickness (mm)	Thermal conductivity (W/m·K)	Thermal expansion coefficient ($^{\circ}\text{C}^{-1}$)
Porcelain hand mold fired at 1230°C	0.0104 ± 0.0005	0.2736 ± 0.0003	3.5596×10^{-6}
Porcelain hand mold fired at 1270°C	0.0103 ± 0.0005	0.2492 ± 0.0003	5.8570×10^{-6}
Bone china hand mold fired at 1230°C	0.0096 ± 0.0005	0.2953 ± 0.0003	5.3346×10^{-6}
Bone china hand mold fired at 1270°C	0.0087 ± 0.0005	0.2263 ± 0.0003	6.9230×10^{-6}
Commercial ceramic hand mold	0.0104 ± 0.0005	0.2736 ± 0.0003	5.8494×10^{-6}

Remark:

Thermal expansion coefficient of $\text{Al}_2\text{O}_3 = (7.5-8.0) \times 10^{-6} (^{\circ}\text{C}^{-1})$

Theoretical thermal expansion coefficient of bone china = $(6.5-7.2) \times 10^{-6} (^{\circ}\text{C}^{-1})$

Theoretical thermal expansion coefficient of porcelain = $(7.0-14.0) \times 10^{-6} (^{\circ}\text{C}^{-1})$

Theoretical thermal conductivity of porcelain = $0.2500 \text{ W/m}\cdot\text{K}$

Heat capacity of $\text{Al}_2\text{O}_3 = 775 \text{ J/Kg}\cdot\text{K}$

Heat capacity of $\text{SiO}_2 = 740 \text{ J/Kg}\cdot\text{K}$

Heat capacity of porcelain = $1070-1085 \text{ J/Kg}\cdot\text{K}$

Heat capacity of bone china = $850 \text{ J/Kg}\cdot\text{K}$

Table 8: Mean surface tension ($\pm$ SD) of natural and synthetic rubber latex compounds for preparation glove films

Measuring time (seconds)	Surface tension of natural rubber latex compound ^a (mN/m)	Surface tension of synthetic rubber latex compound ^b (mN/m)
0	35.79 ± 0.46	47.32 ± 2.21
0.1	35.86 ± 0.48	48.18 ± 2.32
0.2	35.92 ± 0.37	48.71 ± 2.58
0.3	36.06 ± 0.38	49.40 ± 2.76
0.4	36.13 ± 0.30	49.93 ± 2.82
0.5	36.23 ± 0.33	50.10 ± 2.84
0.6	36.37 ± 0.29	50.18 ± 2.88
0.7	36.40 ± 0.24	50.26 ± 2.97
0.8	36.43 ± 0.25	50.26 ± 2.97
0.9	36.50 ± 0.21	50.30 ± 2.91
1.0	36.54 ± 0.20	50.18 ± 2.86
1.1	36.54 ± 0.24	50.14 ± 2.89
1.2	36.60 ± 0.15	50.01 ± 2.89
1.3	36.64 ± 0.17	49.93 ± 2.89
1.4	36.64 ± 0.17	49.85 ± 2.88
1.5	36.67 ± 0.17	49.77 ± 2.86
1.6	36.67 ± 0.11	49.73 ± 2.89
1.7	36.64 ± 0.17	49.61 ± 2.85
1.8	36.60 ± 0.15	49.52 ± 2.92
1.9	36.57 ± 0.13	49.36 ± 2.85

Table 9: Comparison of contact angle values between natural and synthetic rubber latex droplet on ceramic hand mold surfaces coated with calcium chloride (CaCl_2) made of eggshell

Sample	Contact angle of a natural rubber latex compound droplet on mold surface ($^\circ$)	Contact angle of a synthetic rubber latex compound droplet on mold surface ($^\circ$)
Porcelain hand mold fired at 1230°C	35.3 ± 4.0	33.6 ± 5.0
Porcelain hand mold fired at 1260°C	37.4 ± 8.2	37.8 ± 9.9
Porcelain hand mold fired at 1270°C	51.9 ± 2.3	42.5 ± 6.1
Porcelain hand mold fired at 1280°C	29.4 ± 4.4	42.9 ± 3.7
Porcelain hand mold fired at 1300°C	27.5 ± 7.4	33.9 ± 7.7
Bone china hand mold fired at 1230°C	59.6 ± 4.7	44.1 ± 4.1
Bone china hand mold fired at 1260°C	57.5 ± 6.7	48.6 ± 3.2
Bone china hand mold fired at 1270°C	49.4 ± 6.9	52.6 ± 3.7
Bone china hand mold fired at 1280°C	44.9 ± 5.3	52.7 ± 4.6
Bone china hand mold fired at 1300°C	30.4 ± 4.5	59.9 ± 4.9
Commercial ceramic hand mold	43.4 ± 2.3	50.7 ± 4.0

3.3 Surface Tension and Contact angle of Natural and Synthetic Rubber Latex Compounds on Ceramic Hand Mold Surface

The surface tension data for both natural and synthetic rubber latex compounds at different measuring times is shown in Table 8. The synthetic rubber latex compound had surface tension values higher than in the natural rubber latex compound for all measuring times. Synthetic rubber contains both double bonds and triple bonds which are unsaturated bonds of acrylonitrile and provide hydrocarbon swelling resistance, high T_g , high hardness, and high tensile strength, but its results in low resilience and poor temperature elastomeric properties [13, 41, 42]. However, both nitrile synthetic rubber and natural rubber latex were prepared by using the same system of accelerated sulfur vulcanization process with titanium dioxide filler. Both natural and synthetic rubber latex are suitable for rubber-latex glove film formation by dipping process.

Table 9 shows the contact angle values of natural and synthetic rubber-latex compound droplets on the different firing temperatures of porcelain and bone china hand molds. The sintering temperature of the fired clay hand molds affected the porosity of the mold surface and adherence of the rubber film on mold surface, which in turn affects the contact angle due to wettability and spreading. When the sintering temperature of porcelain hand mold increased, the contact angle of latex droplet on porcelain hand mold surface had trend to increase. However, if the firing temperature of the porcelain hand mold exceeded 1270°C , the contact angle of the natural rubber la-

Figure 8: Contact angles of latex droplets on ceramic hand mold surfaces coated with CaCl_2 from eggshell: a) natural rubber latex droplet on porcelain mold fired at 1270°C ; b) synthetic rubber latex droplet on porcelain mold fired at 1270°C ; c) natural rubber latex droplet on bone china mold fired at 1270°C ; d) synthetic rubber latex droplet on bone china mold fired at 1270°C ; e) natural rubber latex droplet on commercial ceramic hand mold; f) synthetic rubber latex droplet on commercial ceramic hand mold

tex droplet decreased gradually due to quality of porcelain hand molds. For the bone china hand mold, increasing the sintering temperature, decreased the contact angle of natural latex droplets on the bone china mold surface; whereas increasing the sintering temperature increased the contact angle of the synthetic latex droplet on the bone china mold surface due to the high alumina content reported in Table 3 and the different surface tensions between the natural and synthetic rubber latex compounds consistent

Figure 9: Contact angle vs. spreading time of natural rubber latex droplet on the ceramic hand mold surfaces

with the result in Table 8. The contact angle values of natural and synthetic rubber latex compound droplets on fired clay hand molds (porcelain, bone china and commercial ceramic hand molds) are presented in Table 9 and shown in Figure 8. The contact angle values in the range $0^\circ < \theta < 90^\circ$ indicate high wettability [41, 42]. The mean contact angles ($\pm$ SD) of natural and synthetic rubber latex droplets on the commercial ceramic hand mold surfaces were $43.4^\circ \pm 2.3^\circ$ and $50.7^\circ \pm 4.0^\circ$, respectively. The mean contact angles ($\pm$ SD) of natural and synthetic rubber latex droplets on the porcelain hand mold surfaces fired at 1270°C were $51.9^\circ \pm 2.3^\circ$ and $42.5^\circ \pm 6.1^\circ$, respectively. While the mean contact angles ($\pm$ SD) of natural and synthetic rubber latex droplets on the bone china hand mold surfaces were $44.9^\circ \pm 6.9^\circ$ and $52.7^\circ \pm 3.7^\circ$, respectively. The larger contact angle is better than the smaller contact angle because it means good film adhesion on hand mold surface at the same dipping time 15 s. Therefore, in summary, the optimum firing temperature of porcelain and bone china hand molds is an important factor in the stability of the latex droplet, the coating on the fired porcelain and bone china hand molds, and on thin and thick latex glove film formation as shown in Figure 9. Furthermore, CaCl_2 acted as a coagulant is an important factor to allow homogeneous and good adherence of the film formation on the ceramic hand mold surface.

4 Conclusions

Fired porcelain and bone china can be used as hand molds for rubber latex glove film preparation for medical, household, and industrial applications. Porcelain hand molds

fired at 1270°C had good compressive strength, flexural strength, thermal conductivity, and low thermal expansion coefficient of 179.4 MPa, 86.0 MPa, 0.2492 ± 0.0003 W/m·K, and 5.8570×10^{-6} ($^\circ\text{C}^{-1}$), respectively, while bone china hand molds fired at 1270°C had values of 128.4 MPa, 73.7 MPa, 0.2263 ± 0.0003 W/m·K, and 6.9230×10^{-6} ($^\circ\text{C}^{-1}$), respectively. The thermal expansion coefficient of the fired porcelain hand molds was lower than for the fired bone china hand molds due to high percentage of silica (SiO_2) 64.70%wt but the low alumina (Al_2O_3) 22.60%wt content. Amount of cation (Al^{3+} and Si^{4+}) affects on heat transport by atomic vibration in its structure. Thermal conductivity of ceramics depends on their ability of heat capacity, heat convection and heat radiation effect to atomic vibration. However, the contact angle results for both natural and synthetic rubber latex compound droplets on the fired porcelain and bone china hand molds with calcium chloride (CaCl_2) coagulant made of eggshell had good stability and wettability on the hand mold surfaces due to $0 < \theta < 90^\circ$. The thickness of the latex film for hand glove preparation depended on types of ceramic hand molds and the dipping time. A high contact angle and long dipping time influenced the latex glove film thickness, whereas a low contact angle and short dipping time resulted in thin films. In addition, the contact angle values of natural and synthetic rubber latex droplets resulted in different surface tension values for the natural and synthetic rubber latex compounds.

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