Chemical Composition, Zeta Potential, Surface Tension and Contact Angle of Rubber Latex on Glazed/Unglazed Porcelain Hand Mold Surface Effect to Physical and Mechanical Properties of Rubber Latex Glove Films

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Abstract: There are many factors effect to physical, chemical and mechanical properties of rubber latex glove film formation, i.e., types of hand mold (glazed and unglazed molds) and rubber latex compound (synthetic and natural rubber latex) dipping time, curing temperature, zeta potential, surface tension, contact angle. Enhancing wettability can promote the spreading of rubber latex over a desirable hand mold surface. The best condition of hand mold preparation is unglazed porcelain fired at 1250°C. The main composition of obtained porcelain hand mold composed of 63.741 wt.% SiO_2, 25.595 wt.% Al_2O_3 and 3.640 wt.% K_2O. The obtained porcelain hand mold for rubber latex film formation has high compressive and flexural strengths, low thermal conductivity, low thermal expansion coefficient and good chemical corrosion resistance equal to 86.0 MPa, 179.4 MPa, 0.2492±0.0003 W/m.K, 5.8570×10^{-6} (°C)and 0.3870 wt.%, respectively. Natural rubber latex compound has surface tension lower than that of synthetic rubber latex compound. Therefore, surface tension values of rubber latex compound droplets affect to the contact angle on the porcelain hand mold surface. The contact angle of a synthetic rubber latex compound droplet on hand mold surface is higher than that of a natural rubber latex compound droplet on the same hand mold surface. The low contact angle can increase rubber latex film formation effect to obtain high tensile strength, elongation at break and film thickness. Furthermore, the long dipping time affects to high film thickness also.

Key words: Porcelain hand molds, rubber latex glove films, wettability, contact angle, Bangkok

INTRODUCTION

The natural rubber latex or NRL has been widely used to produce commercial products many decades. Surgical gloves, household gloves and condoms are some common examples. A well-known property required of the products is the protection against micro-organisms such as bacteria and viruses. In the formation process the NRL is mixed with various chemical substances such as stabilizer agents, crosslink agents or vulcanizing chemicals, accelerators anti-degradation and fillers suitable and required for the natural rubber latex film formation via coagulation and coalescence processes (Yip and Caciol, 2002; Ihalainen *et al.*, 2010). When natural rubber latex compound is deposited on a hand mold surface and then evaporation is allowed to proceed, a continuous, homogeneous film is formed under appropriate conditions. This process is called film formation. The latex film formation relates to evaporation of water and particle ordering, particle deformation and inter-diffusion of polymers across

particle-particle boundaries (Keddie, 1997). Natural rubber latex is a colloidal system of cis-1, 4-polyisoprene particles dispersed in an aqueous serum. The milky white fluid consists of approximately 34% rubber cis-1, 4 polyisoprene, 2-3% proteins, 0.1-0.5% sterol glycosides, 1.5-3.5% resins, 0.5-1.0% ash, 1.0-2.0% sugars and 55-65% water (Cacioli, 1997). Therefore, there is negatively charged phospholipid protein content effect to protein allergy problem (Cacioli, 1997). The process of eliminating excess chemicals such as residual coagulant and some extractable proteins in the NRL compound is by a washing or leaching process during the wet-gel or pro-cure step prior to the vulcanization process. The hand mold is dipped into the NRL compound, leached with circulating warm water and then cured at optimum temperatures in the range of 120-140°C and with optimum times of 10-30 min in an oven to obtain the natural rubber latex gloves with required physical and mechanical properties. After the vulcanization process the product is called a dry-gel or post-cure or the natural rubber latex glove (Yip and Caciol, 2002; Ihalainen *et al.*, 2010; Islam *et al.*, 2012;

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Aldlyami *et al.*, 2010; Njoya *et al.*, 2012). In general, the isoelectric point of natural rubber latex is approximately 3.9-4.6, depending on the type of proteins on surface of the natural rubber latex particles (Bowler, 1953). The coagulant using can reduce the pH below 5. However, it has been found the pH No. <6-7 due to bacterial oxidation of carbohydrates in the serum to form protein-phospholipid complex (Rippel *et al.*, 2003). There are many methods to reduce the allergic problems, i.e., washing with excess water, digestive enzymes, centrifugation to separate protein out, coating or grafting with polymer or powder onto film surface, i.e., polyurethane, polyethylene oxide, poly (acrylamide acrylic acid), talc, lycopodium, calcium carbonate, starch and modified starches. Powdered gloves are widely accepted use for latex gloves by carefully controlling the type and amount. Furthermore, using powdered gloves are still to increase mechanical-physical properties, tactility and ease of donning and removal. Ye and Singh (2000) reported calcium ions (Ca^{2+}) in terms of Calcium Chloride ($CaCl_2$) influence on adsorption behavior of whey proteins at the oil-water interfaces. Now a day the green industries and environmental consciousness are concerned gradually. Sustainable development and eco-efficiency are focused to the majority of every country (Thakur *et al.*, 2010, 2012; Singha and Thakur, 2008, 2009). Most of researchers pay attention to use the bio-materials, green materials, nontoxic materials and recycle materials, i.e., biological wastes, bio-fibers, industrial wastes and biodegradable materials as a starting material to do researches (Thakur *et al.*, 2010, 2012; Singha and Thakur, 2008, 2009). Therefore, this study focuses on adding calcium carbonate from hen eggshell acted as a powder to reduce allergic problem and as a filler to increase mechanical and physical properties of natural rubber latex films.

The objective in this study is to prepare the porcelain hand molds from Thai porcelain clay compare to the commercial hand molds imported from other countries in order to reduce importation in the future. Both of commercial and prepared glazed/unglazed porcelain hand molds are used for natural and synthetic rubber latex glove films formation by dipping process. The fired porcelain ceramic hand molds are suitable performer to prepare natural and synthetic rubber latex glove films due to durability, long life, acid-base durability, low prices, many designs, good thermal resistance and high strength. Furthermore, zeta potential, physical and mechanical properties (dimensional, color, smoothness, size, water penetration, tensile strength and elongation at break) chemical composition and functional group microstructure and contact angle of raw materials, hand molds and rubber latex glove films are analyzed by zeta analyzer, tensile

testing, XRD, FTIR, SEM and contact meter, respectively and measured according to the TIS 1056-2540 and ASTM D 412.

MATERIALS AND METHODS

Experimental: Commercial hand molds were supplied from advanced ceramic company, Bangkok, Thailand. Concentrated natural rubber latex (60%) was supplied by the rubber research institute, chatujak, Bangkok, Thailand.

Nitro-synthetic rubber latex compound was supplied by Bangkok synthetic rubber, rayong province, Thailand. Nitro-synthetic rubber latex composed of dry weight content: nitrile latex 100 part, 3% KOH 1.50 part, sulfur 1.10 part, ZnO 1.30 part, ZDBC 0.70 part, TiO_2 1.50 part and water 15%.

Potassium hydroxide (KOH) is very high purity 90% in solid white color and odorless purchased from chemipan corporation Co., Ltd. Zinc oxide (ZnO) was supplied by Thai-Lysaght Co., Ltd. Zinc oxide is very high purity more than 99.5%, a colorless crystalline compound and not soluble in water.

Sulfur (S) is a solid crystal in yellow color, 99.9% purity and supplied by miwon chemicals Co., Ltd. Sulfur was used as vulcanizing agent dosage 0.3-2.5 phr on dry basis in the form of 50% in dispersion in water. Teric 16A16 was supplied by GSP Products Co., Ltd.

Zinc diethyl dithiocarbamate (ZDEC, $C_{10}H_{20}N_2S_4Zn$) is solid powder 97.0% purity in white to off-white color. ZDEC acted as a fast primary or secondary accelerator in natural rubber latex in white powder having density at 20°C (1.48 g/cm³).

Wingstay L (WSL) is a solid white powder supplied by OMNOVA Engineered Surfaces Co., Ltd. Wingstay L acts as an antioxidant for latex compounding. Titanium dioxide (TiO_2) is a white and odorless powder purchase from Pretiox.

Zinc-2-Mercaptobenzthiazole (ZMBT) was supplied by Nocil. ZMBT is 50% purity and slight amber to brown color liquid. ZMBT is zinc 2-mercaptobenzothiazole ($C_{14}H_8N_2S_4Zn$) used in latex vulcanization having light yellow powder, density at 20°C (1.65-1.72 g/cm³), hardly soluble in acetone, benzene, ethanol and carbon tetrachloride, insoluble in water and gasoline and decomposed in strong acid and alkaline.

Calcium nitrate ($Ca(NO_3)_2$) is 99.0% purity and white powder supplied by Ztum Co., Ltd. The 35 % calcium nitrate was used as a coagulant prepared by mixing 5.8 g of 50% calcium carbonate, Teric 1.2 g and water 59.81 g. Valtamal and bentonite are very purity 100% purchased from interchem Co., Ltd.

Fired glazed and unglazed porcelain hand molds prepared and used as a researching hand mold for synthetic and natural rubber latex gloves preparation by dipping process. Phosphate Buffer Saline (PBS) acted as a buffer solution was prepared from sodium chloride (NaCl) 8.0 g mixed with potassium chloride (KCl) 0.2 g, sodium hydrogen phosphate (Na$_2$HPO$_4$) 1.25 g and potassium hydrogen phosphate (KH$_2$PO$_4$) 0.2 g used for soluble protein testing.

Instruments: X-Ray Diffraction (XRD) data were taken and analyzed using an analyzer (Bruker, D8 discover) with a VANTEC-1 detector and a double-crystal wide-angle goniometer. Scans were obtained from 10-80°2θ at a scan speed of 2°2θ/min in 0.02°2θ increments using CuKα radiation (λ = 0.154 nm). Peak positions of samples are compared with standard JCPDS files to identify the crystalline phases.

Cumulative and fractional distribution was measured by using a particle size analyzer (Mastersizer S long bed, model polydisperse 2.19). The samples were dispersed in a water medium and vibrated in an ultrasonic cleaner for 20 min.

True density of samples was measured according to the ASTM B212-72 by gas pycnometer (quantachrome, ultra pycnometer 1000) for clay and ceramic hand mold. True density of clay powder and fired glazed/unglazed porcelain was calculated according to the ASTM C 373-72 as following Eq. 1:

$$\rho = \frac{Weight(D)}{True\,volume} \tag{1}$$

Where:
ρ   = Bulk density
D   = Weight of dry sample (g)
True volume = The volume of the solid component only

It may be determined by crushing the piece into powder form so that all pores are destroyed and then using a gas pycnometer method for powder. SEM micrographs obtained by using a Scanning Electron Microscope (SEM, JEOL-5200). The samples were mounted on a stub using carbon paste and were sputter-coated to~0.1 μm of gold to improve conductivity. An acceleration voltage of 13-20 kV with magnification in the range of 150-500 times was used.

The specific surface area the pore size and the surface distributions were measured using an AUTOSORB-1 (QUANTACHROME) by determining the quantity of gas adsorbed onto or desorbed from the solid surface at some equilibrium vapor pressure by the static volumetric method. The AUTOSORB-1 has the capability of measuring adsorbed or desorbed volumes of nitrogen at relative pressures in the range 0.001 to slightly below 1.0. When krypton and the micro-pore options are added, the lower limit is extended to 1×10^{-6} and data points can be obtained at 1×10^{-7}. This volume-pressure data can be reduced by the AUTOSORB-1 software into the BET (Brunauer-Emmet-Teller) surface area (single and/or multipoint) the pore size and surface area distributions the micro-pore volume and the surface area using an extensive set of built-in data reduction procedures. The specific surface area, S of the solid can be calculated from the total surface area and the sample weight, according to Eq. 2 and 3 as follows:

$$S = S_t/W \tag{2}$$

$$S = \frac{W_m N A_{cs}}{M} \tag{3}$$

Where:
S   = The specific surface area of the solid
S$_t$ = The total surface area
W   = The sample weight
N   = Avogadro's number (6.023×10^{23} molecules/mol)
M   = The molecular weight of the adsorbate
A$_{cs}$ = The area occupied by one adsorbate molecule (16.2×10^{-20} m^2 for N$_2$ and 19.5×10^{-2} m^2 for Kr)

There are three types of porosity classifications by gas adsorption pores with openings exceeding 500 Å in diameter (called "macropores"), "micro-pores" which describes pores with diameters not exceeding 20 Å and pores of intermediate size (called "meso-pores"). Mechanical properties (tensile strength and elongation at break) were measured according to the TIS 1056-2540 and ASTM D 412 as shown in Fig. 1.

Porcelain pot mill model RM 1105 with speed 500 rpm was supplied by Compound Clay Co., Ltd., Thailand. The pot mill composed of a porcelain pot and porcelain balls ground by electric motor for mixing the clay slurry in order to prepare the porcelain hand mold. The chemical composition of porcelain clay and commercial porcelain hand molds were measured by XRF as the data tabulated in Table 1.

Oven was used to dry the hand mold at 100°C for 24 h and cure the latex glove films preparation at 120°C for 30 min. The highest temperature of oven is 200°C WTB binder, 78532 Tuttlingen. Fourior Transformation Infrared Spectroscopy (FTIR) was used to record with a spectrometer (perkin elmer, spectrum one) at a spectral resolution of 4/cm. The samples were measured in the
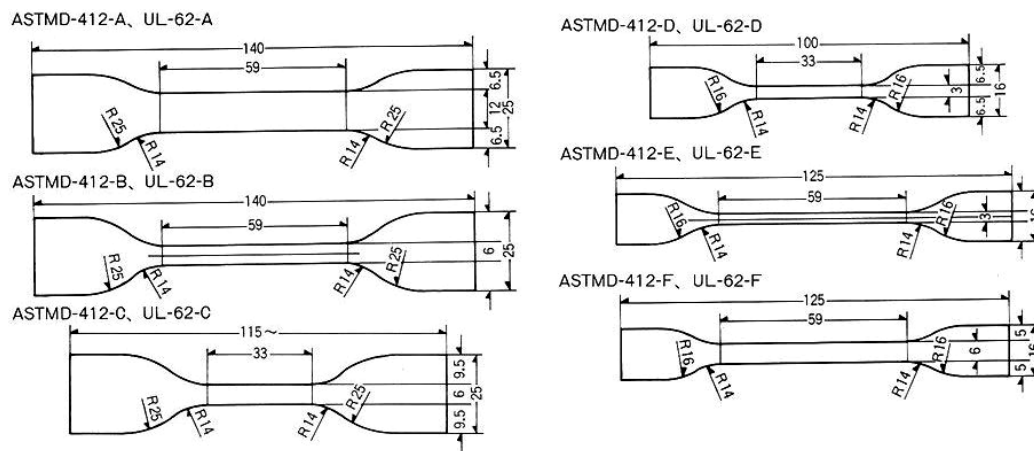
Fig. 1: Samples preparation for the mechanical property testing according to ASTM D412

Table 1: Comparison of chemical composition of raw porcelain clay and commercial hand molds

Chemical composition (wt.%)	Commercial hand molds	Porcelain clay
Na_2O	1.689	3.109
MgO	0.272	0.196
Al_2O_3	25.595	27.731
SiO_2	63.741	64.439
P_2O_5	0.181	0.127
SO_3	0.174	0.194
K_2O	3.640	2.700
CaO	1.479	0.345
TiO_2	0.431	0.077
Fe_2O_3	1.343	0.854
Rb_2O	0.109	0.050
ZrO_2	0.088	0.016
SrO	0.468	-
BaO	0.565	0.162
Y_2O_3	0.015	-
Nb_2O_5	0.013	-
Cs_2O	0.168	-
ZnO	0.031	-

range 400-4000/cm by using single-crystal potassium bromide, KBr as a reference. Contact angle was measured by using a contact angle meter (kyowa, model DM-CE 1). The NRL and synthetic compound droplet was deposited onto a porcelain mold surface and images were captured continuously at an interval. Then, the steady state contact angle was analyzed and calculated.

Zeta potential was measured by using a zeta potential analyzer (Malvern, model Zetasizer Ver. 7.04) the magnitude of the electrostatic or charge repulsion/attraction between particles. Zeta potential is one of the fundamental parameters known to affect stability useful for colloidal dispersion and phenomena in the colloid particles in liquid. Its measurement brings detailed insight into the causes of dispersion, aggregation of flocculation and can be applied to improve the formulation of dispersions, emulsions and suspensions.

Furthermore the zeta potential is used to observe the behavior of dispersion systems in liquid, i.e., latex and electrical double layer on the solid/liquid interface (mold surface/latex film formation) a fact very important in flotation and flocculation processes.

Simultaneous thermal analyzer, STA model NETZSCH STA 449F3 measured in the range of 25-1000°C with a heating rate 10°C/min in air was used to characterize %weight loss, thermal reaction, endothermic-exothermic reactions.

Dilatometer model Netzsch: DIL 402 in the range of 30-1200°C with a heating rate 10°C/min was used to measure thermal expansion coefficient and shrinkage of materials. Acid-base resistance was characterized by immersing hand molds into 5% hydrochloric (HCl) and 10% sodium hydroxide solution (NaOH) at temperature 25, 30, 50, 60, 70 and 80°C at each temperature for 18 h. After immersion in acid-base solution the samples were weighed and analyzed defect and fracture.

Porcelain hand molds preparation: The chemical composition of raw porcelain clay of Thailand analyzed by XRF is shown in Table 1. Porcelain clay mixed with water by the ratio 2:1 and then stirred vigorously to obtain slip or slurry. The slip was added small amount 1-2 cm^3 sodium silicate acted as a deflocculant to prevent porcelain clay agglomeration. The obtained slip was poured into plaster researching hand molds for 20-30 min, drained the slip out of the hand mold and let it setting. The porcelain hand molds were casted out of the plaster researching hand molds, let it dry before put in oven for 24 h and fired at high temperature.

Table 2: Formula of natural and synthetic rubber latex compounds for preparing rubber latex glove films

Chemical substances	Weight (g)	Chemical substances	Weight (g)
60% natural rubber latex	167.0	Synthetic nitrile rubber latex	100.00
10% KOH	2.0	3% KOH	1.50
10% Terric 16A16	0.2	Sulfur	1.10
50% Sulfur	1.6	ZnO	1.30
50% ZDEC	0.8	ZDBC	0.70
50% Wingstay	2.0	TiO_2	1.50
50% ZMBT	0.8	H_2O	150.00
50% TiO_2	2.0		
50% ZnO	2.0		
H_2O	170.5		

Natural and synthetic rubber latex films preparation: Porcelain hand molds were first cleaned and dried. Calcium Nitrate $(Ca(NO_3)_2)$ was used as the coagulant. The main functions of a coagulant were to help in the pre-dip solution to convert the liquid latex film to wet-gel on the mold and to improve release properties of the latex films from the molds. Furthermore, $Ca(NO_3)_2$ as a coagulant allowed good and homogeneous film formation. The dipping time of the coagulant was 3 sec. After the hand molds were dipped into the natural and synthetic rubber latex compounds as the formula tabulated in Table 2 for 1, 3 and 5 min then withdrawn slowly and dried at room temperature. The NRL films covered along with the porcelain hand mold were cured in an oven at 120°C for 30 min, allowed to dry and then detached out from the fired glazed/unglazed porcelain hand molds. They were subsequently characterized for the physical properties (thickness, film surface, color and appearance) optical properties (clearance, crack-free) and mechanical properties (tensile strength, elongation at break and tear resistance).

RESULTS AND DISCUSSION

Physical properties of raw materials for porcelain hand molds preparation: The percentage of chemical compositions comparison of commercial hand mold and raw porcelain clay are measured by XRF as data tabulated in Table 1. The main chemical composition of both samples are Silica (SiO_2), Alumina (Al_2O_3), potassium oxide (K_2O) and Calcium Oxide (CaO), respectively. Raw porcelain clay of Thailand has high percentage of silica (64.439wt.%) and alumina (27.731 wt.%) effect to mechanical properties of fired clay products.

The particle size distribution of raw porcelain clay was measured by particle size analyzer as shown in Fig. 2. The d_{10}, d_{50}, d_{90} and d_{avg} of raw clay porcelain are 1.14, 5.76, 21.20 and 9.07 microns, respectively. The specific surface area and isotherm of raw clay porcelain were

Table 3: Acid-base and zeta potential values of samples

Materials	pH (ab)	Zeta potential (mv)
Natural rubber latex	5.89	-36.70
Commercial glazed hand mold	5.44	-16.10
Raw porcelain clay	5.20	-37.20
Unglazed porcelain hand mold	5.92	-29.90

*a initial pH of natural rubber latex is 5.89. In general the natural rubber latex compound was used to make the latex gloves having the pH 10.5; The $Ca(NO_3)_2$ acted as a coagulant for natural rubber latex glove film formation having the pH 2-3; b initial pH of porcelain slip is 5.92; the zeta potential is a key indicator of the stability of colloidal dispersions. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent, similarly charged particles in dispersion. When the potential is small, attractive forces may exceed this repulsion and the dispersion may break and flocculate. So, colloids with high both negative or positive zeta potential are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate as following these (zeta potential (mV): stability behavior of the colloid) (Singha and Thakur, 2009; Thakur *et al.*, 2010; Tsai *et al.*, 2006; Savaji *et al.*, 2014; Guan *et al.*, 2010; Au and Leong, 2013; Tangboriboon *et al.*, 2012): If the zeta potential value is in the range 0 to ±5, the stability behavior of the colloid is rapid coagulation, precipitation or flocculation; if the zeta potential value is in the range ±10 to ±30, the stability behavior of the colloid is incipient instability and begins to agglomerate; if the zeta potential value is in the range ±30 to ±40 the stability behavior of the colloid is moderate stability; If the zeta potential value is in the range ±40 to ±60 the stability behavior of the colloid is good stability; if the zeta potential value is >±61 the stability behavior of the colloid is excellent stability

characterized by BET as shown in Fig. 3, respectively. The specific surface area of raw porcelain clay is equal to 13.52 m^2/g and the hysteresis isotherm is in the range of mesoporous (460.30 Å) of 20°-500 Å.

Thermal analysis comparison of commercial hand mold and raw porcelain clay measured by STA are shown in Fig. 4, respectively. TGA and DTA curves of both commercial hand mold and raw porcelain clay are the same trend. The residue mass and endothermic-exothermic peak positions of commercial hand mold are 99.98%, at 120, 604.10 and 868.60°C, respectively. While the residue mass and endothermic-exothermic peak positions of raw porcelain clay are 92.39% at 114.90, 509.80 and 885.90°C, respectively due to moisture, organic contents and aluminosilicate formation. For the TGA result it means the porcelain is high thermal resistance.

Zeta potential of samples depends on pH and characteristic of samples as data tabulated in Table 3. The zeta potential is a key indicator of the stability of colloidal dispersions. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent, similarly charged particles in dispersion. When the potential is small, attractive forces may exceed this repulsion and the dispersion may break and flocculate. So, colloids with high both negative or positive zeta potential are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate as following these (zeta potential (mV): stability behavior of the colloid) (Singha and Thakur, 2009; Thakur *et al.*, 2010; Tsai *et al.*, 2006; Savaji *et al.*, 2014; Guan *et al.*, 2010; Au and Leong, 2013; Tangboriboon *et al.*, 2012):
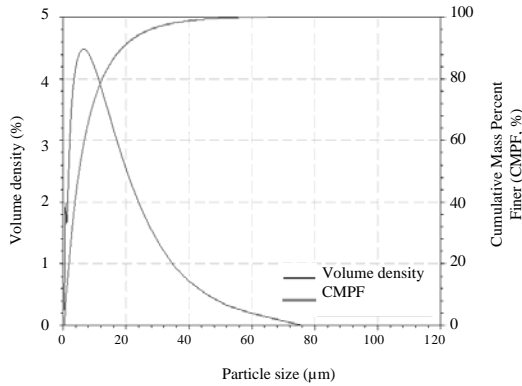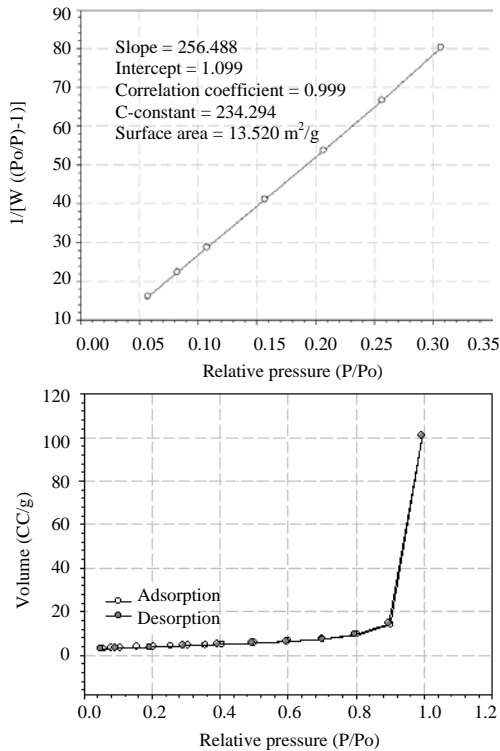
Fig. 2: Particle size distribution of raw porcelain clay

Fig. 3: Specific surface area of raw porcelain clay

- If the zeta potential value is in the range 0 to ±5 the stability behavior of the colloid is rapid coagulation, precipitation or flocculation
- If the zeta potential value is in the range ±10 to ±30 the stability behavior of the colloid is incipient instability and begins to agglomerate
- If the zeta potential value is in the range ±30 to ±40 the stability behavior of the colloid is moderate stability
- If the zeta potential value is in the range ± 40 to ±60 the stability behavior of the colloid is good stability
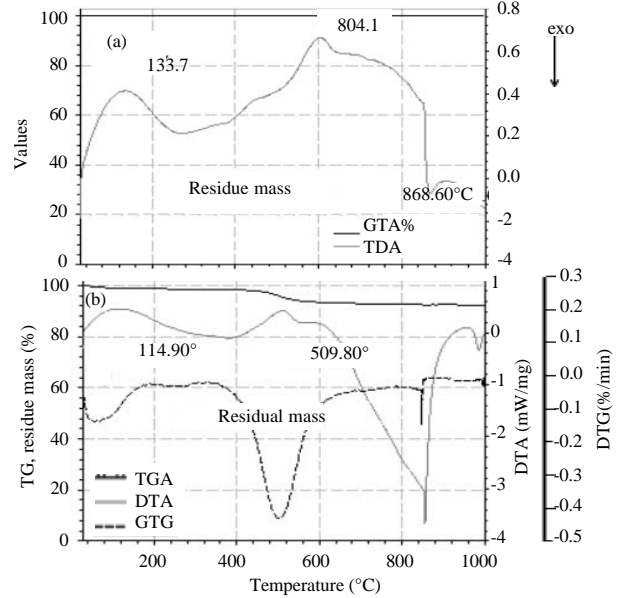

Fig. 4: Thermal analysis of samples: a) commercial hand mold and b) raw porcelain clay

Table 4: Comparison of physical and mechanical properties of commercial and porcelain hand molds

Samples	True density (g/cm³)	Compressive strength (MPa)	Flexural strength (MPa)
Commercial glazed hand molds	2.53	89.20	129.60
Porcelain hand molds fired at 1250°C	2.58	86.00	179.40
White glazed porcelain and fired at 1250°C	2.69	91.10	96.60
Clear glazed porcelain and fired at 1250°C	2.69	17.30	74.50

- If the zeta potential value is more than ±61 the stability behavior of the colloid is excellent stability

Therefore, the good wettability of natural or synthetic rubber latex onto both glazed commercial and porcelain hand molds needs to dip into $Ca(NO_3)_2$ acted as a coagulation for thin film before dip into natural or synthetic rubber latex for glove films preparation. The unglazed hand molds are potential to coagulated the rubber latex better than that of glazed surface consistent with the zeta potential of porcelain hand mold (-29.90 mV) and commercial glazed hand mold (-16.10 mV) in the same range. However, the different zeta potential affects to the obtained rubber film thickness.

Comparison of true density values of commercial glazed hand molds, unglazed porcelain hand molds and white glazed and clear glazed porcelain hand molds are tabulated in Table 4. Commercial glazed and unglazed porcelain hand molds have true density values equal to 2.53 and 2.50 g/cm³, respectively. While, white glazed and
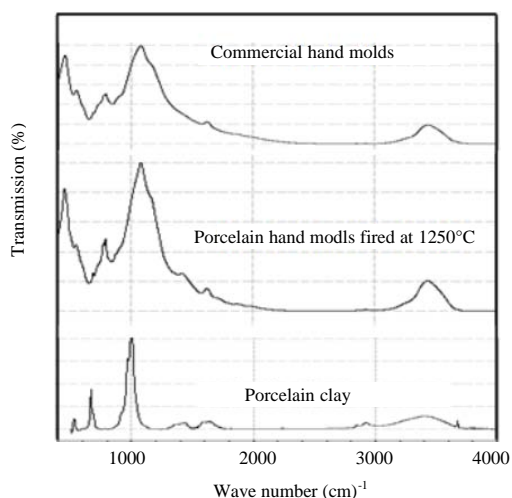
Fig. 5: Comparison of the FTIR spectra between raw clay porcelain and porcelain hand molds fired at 1250°C

clear glazed porcelain hand molds have the same true density values equal to 2.69 g/cm^3. Glazing of hand mold surface can decrease porosity due to glassy phase formation. However, glazing is not good for rubber film formation as an unglazed hand mold due to slither.

Physical properties of porcelain hand molds: FTIR spectra between raw porcelain clay and porcelain hand molds fired at 1250°C are shown in Fig. 5. The FTIR spectra of raw porcelain clay show peaks at 431, 461-471, 648 and 694 cm^{-1} belonging to υ(Al-O) and υ (Al-O-Si). Raw porcelain clay shows υ (Si-O-Si) and $(PO_4)^{3-}$ at the wave number 537-555 cm^{-1}. Furthermore, the FTIR spectra at 1419 and 1625 cm^{-1} belong to υ (C = O), CH_3 of $(CO_3)^{2-}$ asymmetric deformation and strong υ (C = C). There is a broad spectrum belonging to υ (OH) at 3437-3444 and 3695 cm^{-1}. The FTIR spectra of commercial hand mold are similar to those of porcelain hand mold fired at 1250°C belonging to υ (Al-O), υ (Al-O-Si) at 460-471 cm^{-1}. The υ (Si-O-Si) and $(PO_4)^{3-}$ are at 537-555 cm^{-1}. In addition there are υ (Al-O-Si), υ (Si-O), υ (Ca-O-Si) and υ (Ca-O) at 779 and 797 cm^{-1}. There is small spectrum of strong υ (C = C) at 1625 cm^{-1}. The υ (OH) happens at 3437-3444 cm^{-1}.

SEM micrographs of raw clay porcelain and glazed/unglazed porcelain hand molds before and after firing with magnifications of 500X, 5000x and 20000X are shown in Fig. 6. SEM micrographs of raw porcelain clay are agglomeration of fine particle with a plate-like shape as shown in Fig. 5. Therefore, the porcelain slip preparation has to add small amount of sodium silicate for de-agglomeration. After firing porcelain hand mold, the porosity reduced due to densification as shown in Fig. 5. However, unglazed porcelain hand mold still contains small amount of porosity. While both white and clear glazed porcelain hand molds show good densification,

Table 5: Thermal conductivity of samples

Samples	Thickness (mm)	Thermal conductivity (W/m.K)
Porcelain hand molds fired at 1250°C	0.0103±0.0005	0.2492±0.0003
Porcelain hand molds coated white glazed and fired at 1250°C	0.0104±0.0005	0.2736±0.0003
Porcelain hand molds coated clear glazed and fired at 1250°C	0.0102±0.0005	0.2733±0.0003

smooth surface and no porosity due to high glassy phase formation coating on hand mold surface as shown in Fig. 5.

XRD peak patterns of raw porcelain clay, porcelain hand molds before and after firing in the range of 5-80° are shown in Fig. 6. The XRD peaks of raw porcelain clay show at 2θ 6.1894° (100%) 23.7103° (49.5%) 15.7047° (36.9%) 20.9197° (36.4%) and 27.1183° (28.4%) consistent with the JCPDS no. 00-043-0168 belonging to sodium aluminum silicate hydrate ($Na_2Al_2Si_4.5O_{13} \times H_2O$) in cubic phase formation. The XRD peak patterns of commercial hand molds are similar to those of fired porcelain hand molds. The main compositions of both commercial and porcelain hand molds are silica (SiO_2), alumina (Al_2O_3) and mullite ($Al_6Si_2O_{13}$). Furthermore, the highest peak positions of both commercial and porcelain hand molds are 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 no. 00-046-1045 belonging to silica (SiO_2) of hexagonal phase and 00-010-0394 belonging to mullite ($Al_6Si_2O_{13}$) of rhombohedral phase formation.

Mechanical and thermal properties of glazed/unglazed porcelain hand molds compare to commercial hand molds: Unglazed and white glazed porcelain hand molds were measured mechanical properties as data tabulated in Table 5. Unglazed and white glazed porcelain hand molds have the compressive strength values close to the commercial hand mold equal to 86.00, 91.10 and 89.20 MPa, respectively. While clear glazed porcelain hand molds has very low compressive strength 17.30 MPa due to high glassy phase formation on clear glaze or high percentage of silica content in clear glaze. It induces to easily crack after compressive force loading. Flexural strength or bending test of unglazed porcelain hand molds has the highest value 179.40 MPa. Commercial hand molds are 129.60 MPa. While white glazed and clear glazed porcelain hand molds have low flexural strength equal to 96.60 and 74.50 MPa, respectively due to high glassy phase formation on mold surface also.

Thermal properties of unglazed/glazed porcelain and commercial hand molds are data tabulated in Table 5 and 6. Unglazed, white glazed and clear glazed porcelain hand mold have low thermal conductivity equal to 0.2492±0.0003, 0.2736±0.0003 and 0.2733±0.0003 W/m.K, respectively. Thermal expansion coefficient values of
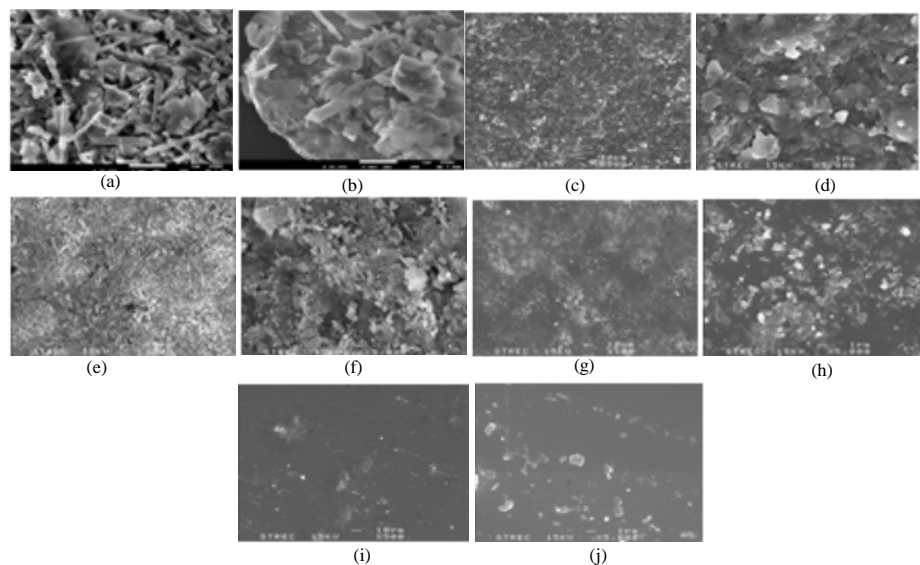
Fig. 6: SEM micrographs of samples with the magnifications of 500, 5000 and 20000X: a, b) raw porcelain clay; c, d) dried porcelain hand mold before firing; e, f) unglazed porcelain hand molds after firing at 1250°C; g, h) white glazed porcelain hand molds after firing at 1250°C; i, j) clear glazed porcelain hand molds after firing at 1250°C, respectively

Table 6: Comparison of thermal properties of commercial and porcelain hand molds

Samples	Thermal expansion coefficient $(\alpha) \times 10^{-6}$ $(°C)^{-1}$	dL/L_0	El(%)
Glazed commercial hand molds	5.8494	2.94×10^{-3}	0.294
Unglazed commercial hand molds	5.9138	2.94×10^{-3}	0.294
Unglazed porcelain hand molds fired at 1250°C	5.8570	3.82×10^{-3}	0.382
Clear glazed porcelain hand molds fired at 1250°C	3.5596	3.57×10^{-3}	0.357

Table 7: Corrosion and weight loss of commercial and porcelain hand molds immersed into 10% NaOH and 5%HCl at 70°C for 18 h

Samples	Weight loss (%)
Commercial glazed hand molds	0.5869
Unglazed porcelain hand mold fired at 1250°C	0.3870
White glazed porcelain hand mold fired at 1250°C	1.2266
Clear glazed porcelain hand mold fired at 1250°C	1.9188

glazed and unglazed commercial hand mold, unglazed porcelain hand mold and clear glazed porcelain hand molds are equal to 5.8494×10^{-6}, 5.9138×10^{-6}, 5.8570×10^{-6} and $3.5596 \times 10^{-6} (°C)^{-1}$, respectively. Thermal expansion coefficient values of commercial and unglazed porcelain hand molds are similar values of porcelain materials except a clear glazed hand mold.

Corrosion or acid-base resistance of glazed/unglazed porcelain hand molds compare to commercial hand molds: Corrosion or acid-base resistance of commercial, unglazed, white glazed and clear glazed porcelain hand molds were measured by dipping samples into HCl and

NaOH solution and then calculating the weight loss as data tabulated in Table 7. Unglazed porcelain hand mold has the lowest percentage of weight loss 0.3870% effect to high corrosive resistance. Whereas the weight loss of glazed commercial hand mold is equal to 0.5869% at the same condition, It means that the obtained unglazed porcelain hand mold is high corrosion resistance. In addition, both white and clear glazed porcelain hand molds are high percentage of weight loss equal to 1.2266 and 1.9188%, respectively. The main composition of glaze is silica that can be corroded by acid-basic solution at high temperature (70-80°C). Therefore, glazed porcelain hand molds have chemical corrosion higher than that of unglazed porcelain hand molds.

Characteristics and contact angles of synthetic and natural rubber latex on unglazed/glazed porcelain hand molds and commercial hand molds: FTIR spectra comparison of synthetic and natural rubber latex for gloves preparation are shown in Fig. 7. The FTIR spectrum of natural rubber latex compounds shows peaks at 533 cm^{-1} (S-O) st., 689 and 834 cm^{-1} δ (C-H), 700 cm^{-1} δ (=C-H) 1013 cm^{-1} strong υ (C-O) and υ (C = S) at 1375 and 1444 cm^{-1}(S = O) st and (C-O) st., 1631 and 1658 cm^{-1} (C = C) st. and (C = O) st., 2853, 2923 and 2960 cm^{-1} (=C-H) st and (=C-H) st., a broad band peak at 3405 cm^{-1} (O-H) st and a small peak at 3675 cm^{-1} υ (O-H) consistent with the FTIR results (Tangboriboon *et al.*, 2012). While the FTIR spectrum of synthetic rubber latex compounds shows peaks at 530 cm^{-1} (S-O) st., 668 cm^{-1}
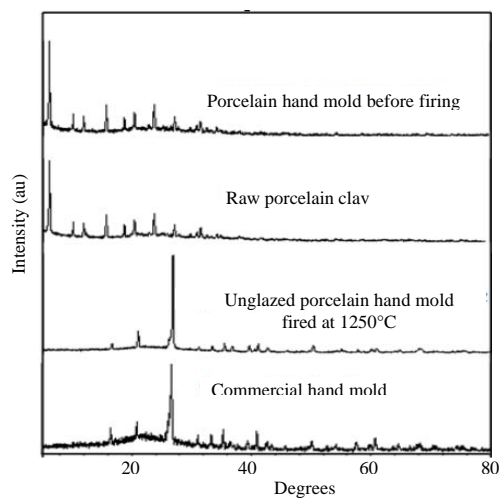
Fig. 7: Comparison of XRD peak patterns of commercial hand mold, raw porcelain clay, dried porcelain hand mold and porcelain hand mold fired at 1250°C
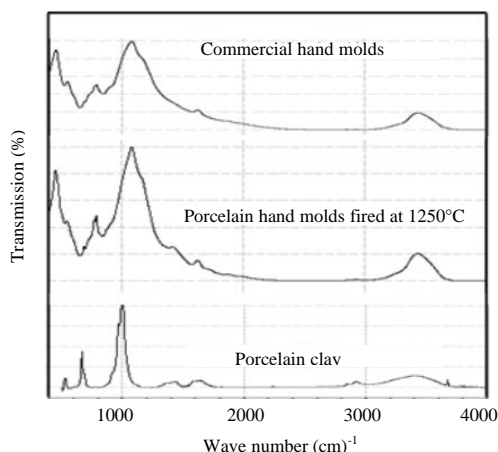

Fig. 8: Comparison of FTIR spectra between natural rubber latex films and synthetic rubber latex films

δ(C-H), 1002 cm^{-1} strong υ (C-O) and υ (C = S), at 1411 and 1630 cm^{-1}, broad band peaks at 2850 cm^{-1} (N = O) st., 2922 and 3407 cm^{-1} (N-H) st and a small peak at 3674 cm^{-1} υ (O-H). The synthetic rubber latex compounds contain nitro-group in their structure differ from the natural rubber latex compounds.

Surface tension is the elastic tendency of a fluid surface which makes it acquire the least surface area possible in terms of force per unit length or surface free energy per unit area. The net effect is an inward force at its surface that causes the liquid to behave as if its surface were covered with a stretched elastic membrane. The surface becomes under tension from the imbalanced forces namely surface tension. In addition, surface tension is an important factor in the capillarity
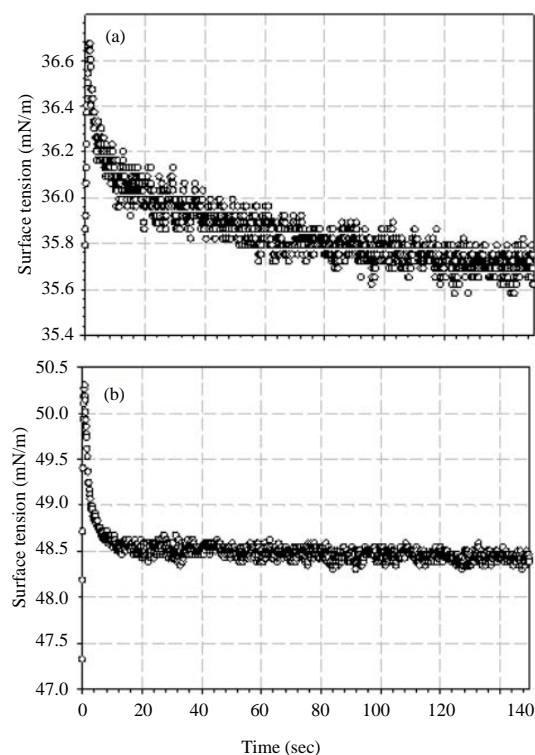

Fig. 9: Comparison of surface tension vs. time of: a) natural rubber latex compound and b) synthetic rubber latex compound

Table 8: Comparison of surface tension of natural and synthetic rubber latex compounds

Time (sec)	Surface tension of natural rubber latex compounds (mNm^{-1})	Surface tension of synthetic rubber latex compounds (mNm^{-1})
0.0	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

phenomenon. Surface tension of synthetic and natural rubber latex compounds are shown in Fig. 8-9 and data tabulated in Table 8. Synthetic and natural rubber latex have surface tension values equal to 50.10 and 35.50 mN/m. Synthetic rubber latex has surface tension

Table 9: Contact angles of natural and synthetic rubber latex compound droplets on commercial and porcelain hand mold surfaces

Samples	Natural latex compounds (°)	Synthetic latex compounds (°)
Unglazed commercial hand mold surface	43.5±2.3	50.7±4.0
Glazed commercial hand mold surface	42.1±3.7*	53.0±4.6
Unglazed porcelain fired at 1250°C	33.6±5.0	37.4±8.2
Clear gloss porcelain fired at 1250°C	36.5±5.8	40.9±3.8
White gloss porcelain fired at 1250°C	40.7±4.2	40.9±3.8

Table 10: Mechanical properties of rubber latex glove films

Samples	Dipping time (min)	Max. tensile force (N)	Tensile strength (MPa)	Elongation at break (%)	Film thickness (mm)
Synthetic rubber latex films casted by commercial hand mold[a]	15 sec	7.5250±2.4066	8.3611±2.6740	369.0909±118.5728	0.1500
Natural rubber latex films casted by commercial hand mold[b]	15 sec	13.1900±0.1203	14.6556±0.1337	695.2727±12.01650	0.1500
Synthetic rubber latex films casted by unglazed porcelain hand mold	1	1.815±0.60020	0.9758±0.3227	765.4545±136.2788	0.3100
Synthetic rubber latex films casted by unglazed porcelain hand mold	3	3.1100±0.9865	1.6198±0.5138	943.9393±114.4086	0.3199
Synthetic rubber latex films casted by porcelain hand mold	5	3.8633±0.5859	1.6097±0.2441	1024.0910±137.4222	0.4000
Natural rubber latex films casted by unglazed porcelain hand mold	1	29.9133±5.2263	15.1077±2.6395	1014.6970±96.75770	0.3300
Natural rubber latex films casted by unglazed porcelain hand mold	3	52.3000±2.1071	17.4333±0.7024	1071.8180±25.54770	0.3499
Natural rubber latex films casted by unglazed porcelain hand mold	5	45.8417±8.3000	21.8294±3.9524	1092.7270±3.431800	0.5000

[a, b]commercial synthetic and natural rubber latex films were purchased from drug store and measured as the referent data to compare with the obtained synthetic and natural rubber latex films from dipping porcelain hand molds into natural and synthetic rubber latex compounds for 1, 3 and 5 min., respectively.

values higher than those of natural rubber latex along with the time. There are many reasons effect to latex surface tension, i.e., the percentage of total solid content between synthetic and natural rubber latex equal to 46 and 60%, chemical functional group, pH, particle size, zeta potential, molecular weight of monomer, type of unsaturated bond and chemical substances added into rubber latex compounds, polarity and surface stress (surface energy). Molecular weight values of synthetic and natural rubber latex monomers are 107 and 68 g/mol, respectively. In addition the structure of synthetic rubber latex composed of both double and triple unsaturated bonds effect to high surface tension.

Where the two surfaces meet they form a contact angle which is the angle the tangent to the surface makes with the solid surface. Contact angle is where a concave meniscus has contact angle less than 90°. The contact angle measurement used for wettability characterization of solid surfaces by a liquid or rubber latex compounds. Contact angles of synthetic and natural rubber latex droplets on unglazed/glazed porcelain hand molds and commercial hand molds are tabulated in Table 9. Both natural and synthetic rubber latex droplets on the glazed/unglazed commercial hand mold surface are higher than those of glazed/unglazed porcelain hand mold surfaces. The contact angles of all natural and synthetic rubber latex droplets on hand mold surfaces are in the range of 33-53°. Contact angles of natural rubber latex droplet on glazed/unglazed porcelain hand molds are lower than those of synthetic rubber latex droplet on the same molds. However, both synthetic and natural rubber

latex compounds can still spread on the hand mold surface and good wettability for film formation. Therefore, the rubber latex film thickness depends on the dipping time of hand molds in the rubber latex compounds (Table 10).

Mechanical properties of synthetic and natural rubber latex films by dipping on unglazed/glazed porcelain and commercial hand molds: Natural rubber latex films casted from commercial and unglazed porcelain hand molds are good mechanical properties. The long dipping time of porcelain hand mold into natural and synthetic rubber latex compounds affects to receive high tensile strength, high elongation at break and high film thickness. Thickness, tensile strength and elongation at break of natural rubber latex films made from dipping unglazed porcelain hand mold for 1 min are 0.33 mm, 15.1077±2.6395 MPa and 1014.6970±96.7577%, respectively. While, thickness, tensile strength and elongation at break of synthetic rubber latex films made from dipping unglazed porcelain hand mold for 1 min are 0.31 mm, 0.9758±0.3227 and 765.4545±136.2788%, respectively.

CONCLUSION

The obtained porcelain hand molds were further characterized for the physical-chemical-mechanical thermal properties such as zeta potential, appearance, true density, microstructure, phase composition, chemical composition, chemical functional groups, corrosion

resistances, compressive and flexural strength, thermal expansion coefficient and thermal conductivity. In addition, the obtained rubber latex glove films were further characterized for the physical and mechanical properties such as appearance, film thickness, tackiness, tensile strength and elongation at break were studied and reported here. The unglazed porcelain hand molds fired at 1250°C are suitable for using as a former for rubber latex glove film formation. The obtained hand molds are good compressive and flexural strengths, low thermal conductivity, low thermal expansion coefficient and good chemical corrosion resistance equal to 86.0 MPa, 179.4 MPa, 0.2492±0.0003 W/m.K, 5.8570×10^{-6} $(°C)^{-1}$ and 0.3870 wt.%, respectively. While, the commercial porcelain hand molds have compressive and flexural strengths, thermal expansion coefficient and chemical corrosion resistance equal to 89.2 MPa, 129.6 MPa, 5.9138×10^{-6} $(°C)^{-1}$, 0.5869 wt.%, respectively. Natural rubber latex compound has surface tension lower than that of synthetic rubber latex compound approximately 35.79±0.46 and 47.32±2.21 mN/m, respectively. Surface tension of rubber latex compounds affects to the droplet on the porcelain hand mold surface namely contact angle. The contact angle of synthetic rubber latex compound on hand mold surface are higher than that of natural rubber latex compound at the same hand mold surface. The contact angles of synthetic and natural rubber latex on unglazed porcelain hand mold surface fired at 1250°C are 37.4±8.2 and 33.6±5.0°, respectively. Low contact angle on hand mold surface affects to high tensile strength, high elongation at break and high film thickness due to good wettability or spreading. Tensile strength, elongation at break and tensile stress of natural rubber latex film casted from unglazed porcelain hand mold for 1 min are equal to 15.1077±2.6395 MPa, 1014.6970±96.7577% and 29.9133±5.2263 N, respectively. Whereas tensile strength, elongation at break and tensile stress of synthetic rubber latex film casted from unglazed porcelain hand mold for 1 min are equal to 0.9758±0.3227 MPa, 765.4545±136.2788% and 1.815±0.6002 N, respectively. In addition increasing dipping time of hand molds into rubber latex effect to obtain high film thickness, high tensile strength and high elongation at break. The film thickness values of dipping hand mold into natural rubber latex compounds for 1, 3 and 5 min are equal to 0.3300, 0.3499 and 0.5000 mm, respectively. While, the film thickness values of dipping hand mold into synthetic rubber latex compounds for 1, 3 and 5 min are equal to 0.3100, 0.3199 and 0.4000 mm, respectively.

REFERENCES

Aldlyami, E., A. Kulkarni, M.R. Reed, S.D. Muller and P.F. Partington, 2010. Latex-free gloves: Safer for whom?. J. Arthroplasty, 25: 27-30.

Au, P.I. and Y.K. Leong, 2013. Rheological and zeta potential behaviour of kaolin and bentonite composite slurries. Colloids Surf. A. Physicochem. Eng. Aspects, 436: 530-541.

Bowler, W.W., 1953. Electrophoretic mobility study of fresh Hevea latex. Ind. Eng. Chem., 45: 1790-1794.

Cacioli, P., 1997. Introduction to latex and the rubber industry. French J. Allergology Clin. Immun., 37: 1173-1176.

Guan, B., Q. Ye, Z. Wu, W. Lou and L. Yang, 2010. Analysis of the relationship between particle size distribution of a-calcium sulfate hemihydrate and compressive strength of set plaster: Using grey model. Powder Technol., 200: 136-143.

Ihalainen, P., K. Backfolk, P. Sirvio and J. Peltonen, 2010. Topographical, chemical, thermal and electrostatic properties of latex films. Colloids Surf. A. Physicochemical Eng. Aspects, 354: 320-330.

Islam, O., K.I. Dragnevski and C.R. Siviour, 2012. On some aspects of latex drying-ESEM observations. Prog. Org. Coat., 75: 444-448.

Keddie, J.L., 1997. Film formation of latex. Mater. Sci. Eng. R. Rep., 21: 101-170.

Njoya, D., M. Hajjaji and D. Njopwouo, 2012. Effects of some processing factors on technical properties of a clay-based ceramic material. Appl. Clay Sci., 65: 106-113.

Rippel, M.M., L.T. Lee, C.A. Leite and F. Galembeck, 2003. Skim and cream natural rubber particles: Colloidal properties, coalescence and film formation. J. Colloid Interface Sci., 268: 330-340.

Savaji, K.V., O. Niitsoo and A. Couzis, 2014. Influence of particle/solid surface zeta potential on particle adsorption kinetics. J. Colloid Interface Sci., 431: 165-175.

Singha, A.S. and V.K. Thakur, 2008. Synthesis and characterization of Grewia optiva fiber-reinforced PF-based composites. Intl. J. Polym. Mater., 57: 1059-1074.

Singha, A.S. and V.K. Thakur, 2009. Physical, chemical and mechanical properties of Hibiscus sabdariffa fiber/polymer composite. Intl. J. Polym. Mater., 58: 217-228.

Tangboriboon, N., P. Phudkrachang, L.O. Mulsow, W. Kunchornsup and A. Sirivat, 2013. Removal of water extractable proteins from concentrated natural rubber latex by eggshells. J. Elastomers Plast., 45: 253-269.

Thakur, V.K., A.S. Singha and M.K. Thakur, 2012. Graft copolymerization of methyl acrylate onto cellulosic biofibers: Synthesis, characterization and applications. J. Polym. Environ., 20: 164-174.

Thakur, V.K., A.S. Singha, I. Kaur, R.P. Nagarajarao and Y. Liping, 2010. Silane functionalization of saccaharum cilliare fibers: Thermal, morphological and physicochemical study. Intl. J. Polym. Anal. Charact., 15: 397-414.

Tsai, W.T., J.M. Yang, C.W. Lai, Y.H. Cheng, C.C. Lin and C.W. Yeh, 2006. Characterization and adsorption properties of eggshells and eggshell membrane. Bioresour. Technol., 97: 488-493.

Ye, A. and H. Singh, 2000. Influence of calcium chloride addition on the properties of emulsions stabilized by whey protein concentrate. Food Hydrocolloids, 14: 337-346.

Yip, E. and P. Cacioli, 2002. The manufacture of gloves from natural rubber latex. J. Allergy Clin. Immun., 110: S3-S14.