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ARTICLES

Full Length Research Paper

Development of leucite glass-ceramics for non-metallic dental product

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The objective of this study was to determine the potential of using Malaysian silica sand as the SiO_2 raw material in producing leucite (SiO_2-Al_2O_3-K_2O) glass-ceramics. The crystallization, mechanical and biological properties of the glass-ceramic was studied. A starting glass composition in the system of leucite was melted in an electric furnace, quenched in deionized water and dry milled to obtain glass powder. The glass powders were ball milled and compressed to form 13 mm x 10 mm pellet. The thermal analysis, phase composition, microstructure, flexural strength and cytotoxicity of the glass-ceramics were investigated. Thermal analysis showed that crystallization of the glass occurred at the range of 650 and 850°C. The pellets were sintered at 650, 700, 750, 800 and 850°C for 1.0 h. The effect of sintering time on crystallization was also studied through five different soaking time at 3.0, 6.0, 9.0 and 12.0 h. The crystallization depends on the temperature and time of sintering. At 700°C, leucite began to form with minor phase of sanidine. The peak intensity increased as the temperature was increased up to 850°C. For sintering time 3.0 to 12.0 h, the peak intensity of leucite and sanidine were increased but microcline was formed as a minor phase. The microstructure analysis showed that the dendritic leucite and prismatic sanidine. The leucite glass-ceramics appeared translucent. The flexural strength values (80 to 175 MPa) were comparable with commercial product (112 to 140 MPa). The *in vitro* bioactivity results prove that the leucite glass-ceramics sample can be classified as a bio-inert and non-cytotoxity material and can be used for restorative dental products.

Key words: Silica, glass-ceramics, leucite, sanidine, dental, bioactivity, bio-inert, cyctotoxicity.

INTRODUCTION

Silica sand is the main raw material for production of silicates glass. Glasses in general term are not advanced materials but through refining in composition, heat treatment and manufacturing, glasses can be transformed into a new class of material called glass-ceramics. Glass-ceramics are polycrystalline materials and produced through controlled crystallization during heat treatment process of glass. Currently, the application of glass-ceramics as biomaterial for dental products is growing. For example, leucite glass-ceramics are widely used in dentistry as restorative dental material to fabricate dental inlays, crowns, bridges and veeners prostheses. Leucite

Table 1. Chemical compositions of the silica sand.

Oxide	SiO_2	Al_2O_3	K_2O	Na_2O	TiO_2	CaO	Fe_2O_3
%	99.57	0.11	0.01	0.01	0.05	0.01	0.02

glass-ceramics can be produced by sintering with surface crystallization of the glass powder. This processing route involves melting, quenching, milling of glass frit, and sintering in order to promote crystallization of glass-ceramics. Glass-ceramics based on leucite show exceptional biocompatibility, and good physical, chemical and mechanical properties (Ahmad, 2006; Cattel et al., 2005).

Since the 1990s, efforts to develop biomaterials for restorative dentistry have been concentrated on producing metal-free systems. An important milestone in this respect was reached in the development of glass-ceramics containing leucite (K_2O -Al_2O_3- SiO_2) (Rheinberger, 1997). Glass-ceramics have been successfully used for many years in dentistry to construct crowns and fixed partial bridges due to the properties of high mechanical strength, chemical inertness, wear resistance, aesthetics and low density. Presently, leucite, mica and lithium disilicate glass-ceramics are widely used as restorative materials (Apel et al., 2007). These materials are particularly suitable for fabricating single units such as dental inlays crowns and veneers because of its special optical properties (Lee et al., 1997). The aim of this project was to investigate the effect of using natural Malaysian silica sand as the SiO_2 raw material on the phase crystallization, microstructure, flexural strength, *in vitro* bioactive and cytotoxicity of leucite glass-ceramics.

MATERIALS AND METHODS

Natural silica sand sample was taken from Terengganu. The sample was wet screened and a fraction 75< to <150 μm was prepared in order to comply with the requirement of traditional glass production technology for glass melts. Chemical composition of the silica sand sample was determined by X-ray fluorescence analysis (Rigaku, Japan). The composition weight percent of the starting glass selected for the study was; 64.2% SiO_2, 16.1% Al_2O_3, 11.9% K_2O, 5.1% Na_2O, 1.7% CaO, 0.5% TiO_2 and 0.5% LiO_2. All oxides used were with purity in the range of 90 to 99% from Merck, Germany; Unilab, Australia and Hamburg Chemical. The batches were placed in plastic bottles and mixed using a Heldoph Reax 2 Shaker, Germany for 8.0 h in order to make sure the raw materials were homogenized. Zirconia balls were used as the media in the mixing process. Samples were melted in alumina crucibles in a bottom-loading high temperature furnace (Modutemp, Australia) at 10°C/min to 1450°C and held for 3.0 h, and then quenched in cool water to produce glass frit. The glass powders were milled (Retsch PM-400, Germany) for 1 h and sieved to the required size of less than 75 μm. The crystallization temperature of the glass powder was studied using Differential Thermal Analysis, DTA (Linseis, Germany) with a 10°C/min heating rate at temperature from 25 to 1100°C in a dry air atmosphere. The glass powder was cold pressed using a laboratory hydraulic hand press (Carver, USA) to obtain green compact in the form of cylindrical pellet of 13 mm x 10

mm. Pellets were heat treated in electric furnace (Termo Temp, UK) at 700, 750, 800 and 850 °C at a heating rate of 2 °C/min and 1.0 h soaking time to study the crystallization behaviour of glass. The effect of sintering time on crystallization was also studied through five different soaking time at 3.0, 6.0, 9.0 and 12.0 h.

XRD (D8 Advanced, Bruker, Germany) was used for the identification of the crystalline phases in the glass-ceramics using Cu Kα radiation at a scan speed of 2°/min for 2θ from 10 to 80°. Microstructure studies were done using field emission scanning electron microscopy (FESEM) (Supra 40 VP, Germany). Before viewing with FESEM, glass-ceramics specimens were embedded, polished and etched with 30% hydrofluoric acid for 7 s. The specimens were platinum coated and viewed using the secondary electron detector. The flexural strength of sintered glass-ceramics was measured using three points bending test with bars of 20 mm x 5 mm x 5 mm (INSTRON, UK, 0.5 mm/min displacement).

The biocompatibility of glass-ceramics sample after heat treatment at 850°C for 9.0 h was examined by *in vitro* bioactivity and cytotoxicity test. The *in vitro* bioactivity test was conducted in Kokubo's simulated body fluid, SBF, which contains almost the same inorganic constituent as human body plasma. The sample was brought into contact with SBF fluid for 10 and 20 days. XRD was used to characterize the formation of apatite on the glass-ceramic surfaces. Cytotoxicity of the leucite glass-ceramics was evaluated by testing on extracts of leucite glass-ceramics according to ISO 10993-5:2009(E) and ISO 10993-12:2012(E). American Type Culture Collection L-929 mouse subcutaneous connective tissue fibroblast cells (Mus musculus, NCTC clone 929, CCL-1) were used in this test. Zinc sulphate at 240 μg/ml and complete growth medium were used as the positive and negative control, respectively. The test material was tested in triplicate at concentration of 6.25, 12.5, 25, 50, 100 and 200 mg/ml.

RESULTS AND DISCUSSION

Chemical analysis result of the silica sand is presented in Table 1. The result reveals that the natural silica sand sample is highly pure and contains very low concentrations of impurities. The content of Fe_2O_3 is low. Generally, typical acceptable value of Fe_2O_3 in silicate glass product is between 0.02 to 0.03% (Malaysian Standard MS 701:1981).

The XRD pattern as shown in Figure 1 identifies the main mineralogical content of the silica sand sample to be quartz. Quenching the glass melts in water at room temperature resulted in transparent and colourless glass frit. The XRD pattern of the glass sample as shown in Figure 1 indicates the present of amorphous glass phase and did not show any evidence of crystalline phase in the glass. The DTA result of the quenched glass powder is shown in Figure 2. The DTA was used to identify the glass transition and crystallization temperature of the glass sample. The temperatures behaviour of a glass can provide information of glass-ceramics fabrication.
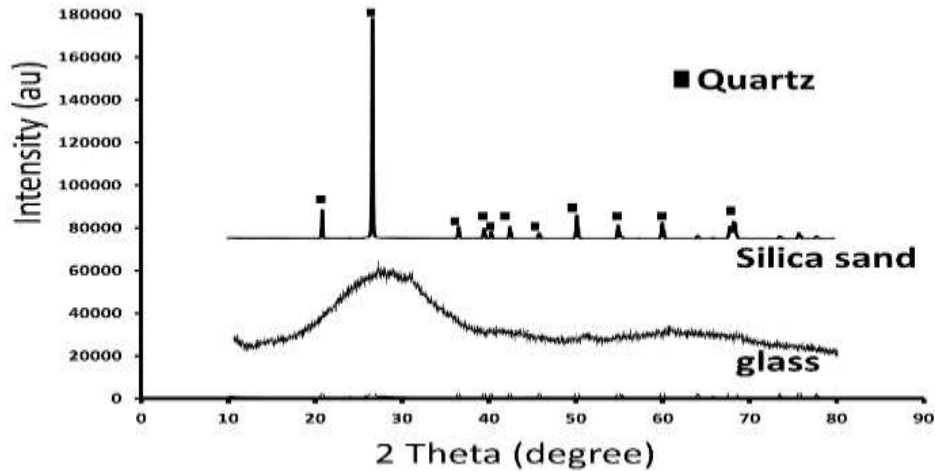
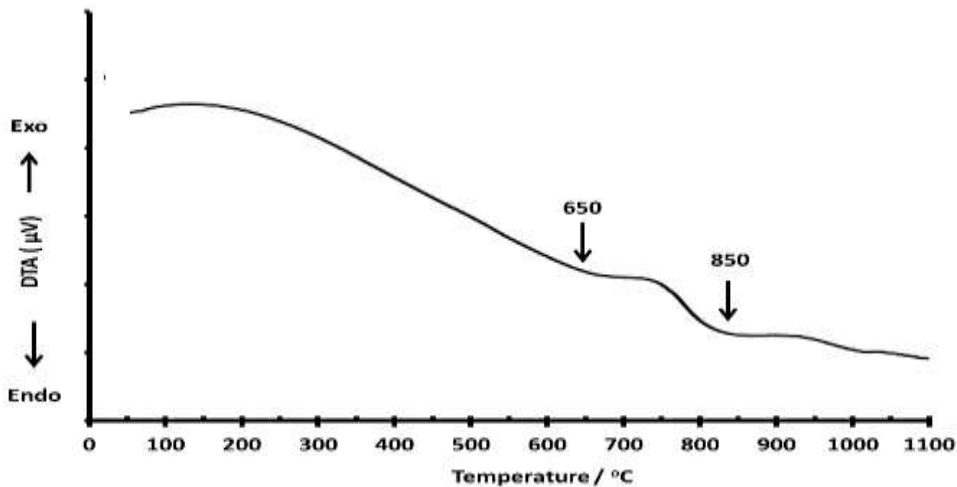**Figure 1.** Powder XRD patterns of the raw silica sand and base glass sample.

Figure 2. DTA curves of the base glass.

According to Sooksaen et al. (2010), the glass transition value of SiO_2-Al_2O_3-K_2O glass system is at about 594 to 638°C (Sooksaen et al., 2010). The DTA curves show that no clear endothermic peak was observed related to glass transition.

However, an exothermic peak associated with the crystallization temperature of glass to form glass-ceramic was in the range of at about 650 to 850°C. Consequently, heat treatment was performed in this study at 700, 750, 800 and 850°C, respectively to form the glass-ceramics, assuming phase evolution was completed at each isothermal hold of 1.0 to 12.0 h.

The glass-ceramics appearance after sintering at 700°C was slightly translucent and white. Increasing the sintering temperature up to 800°C has transformed the samples to become more white and opaque. The XRD patterns of glasses that were heat-treated at 700, 750, 800 and 850°C for 1.0 h are shown in Figure 3. The results indicated the presence of cubic leucite, $KAlSi_2O_6$, (ICDD: 00-038-1423) and sanidine, $(K,Na)(Si_3Al)O_8$, (ICDD: 00-019-1227). It is also proved that the amount of leucite and sanidine phase for each heat-treated glass composition was increased with the increasing of heat treatment temperature.

The effect of sintering time on the crystallization is shown in Figure 4. As the sintering time was increased, all peaks associated with cubic leucite and sanidine became stronger. However, for sintering temperature at 700 and 750°C and soaked 6 h, microcline (ICDD: 00-019-0932) started to form as a minor phase. While for 800 and 850°C microcline started to crystallize within 3.0 h soaking time. The cry stallization of microcline was previously identified in leucite reinforced glass-ceramics in SiO_2-Al_2O_3-K_2O glass system (Chen et al.,
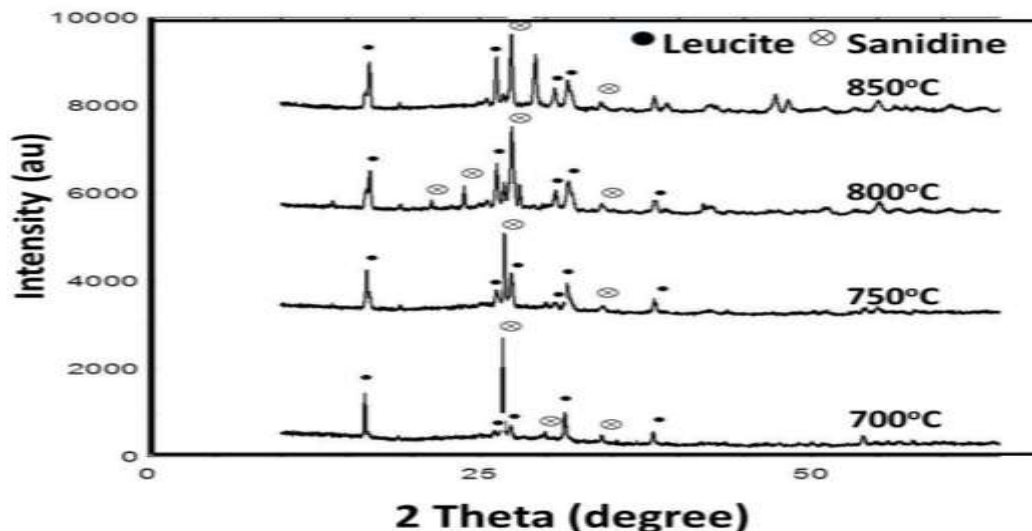
Figure 3. XRD pattern of glass-ceramics sintered at 700, 750, 800 and 850°C for 1 h.

2010). Figure 5 shows the FESEM micrographs of glass-ceramics sample sintered at 850°C for 1.0 h and 9.0 h. The formation of dendritic cubic leucite and prismatic sanidine phases is clearly observed. A previous study by Holand and Beall (2002) on crystallization mechanisms in glass-ceramics showed that the early stages of bulk leucite growth have been due to dendrites growing in preferred crystallographic directions (Holand and Beall, 2002). The micrographs also show there were no obvious micro cracks.

Figure 6 shows the graph of the flexural strength results of the glass-ceramics sintered at 700, 750, 800 and 850°C and soaked at 1.0, 3.0, 6.0, 9.0 and 12.0 h. The flexural strength of leucite glass-ceramics was increased as the time and sintering temperature was increased. It could be due to the high volume of crystalline phases and the existence of prismatic sanidine. The higher flexural strength, 175 MPa was achieved for sample sintered at 850°C for 9.0 h. However, the flexural strength decreased after soaking for 9.0 h at all temperatures. This is probably due to the glass-ceramics which started to melt and part of crystallite began to dissolve in the residual glass phase. The flexural strength values of glass-ceramics samples were comparable with commercial product of which is 112-140 MPa (El-Meliegy and Noort, 2011).

Glass-ceramics for restorative dental applications must fulfill the standard tests for biomaterial use, such as compatibility with the oral environment. Bioactivity on the surface of the dental restoration did not occur in XRD patterns of sintered glass-ceramics before and after soaking in SBF for several days as shown in Figure 7. Patterns show that there is no presence of apatite layer on the surface of glass-ceramics sample after 20 days of immersion in SBF and that indicated the sample is inert

bioactive materials.

In this study, the MTT assay is used to evaluate the toxic characteristics of the leucite glass-ceramics and the yellow tetrazolium salt (MTT) is reduced in metabolically active cells to form insoluble purple formazan crystals which are solubilized by the addition of a solvent (dimethyl sulfoxide). Cell viability is qualified by colorimetric enumeration whereby a low optical density (OD) reading corresponds to low cell viability which is associated with a loss in mitochondrial dehydrogenase activity.

The test material leucite glass-ceramics did not inhibit the viability of L929 cells at all concentrations following 24-hour treatment as shown in Table 2 and Figure 8. Table 2 also shows that at all concentrations of test material, the viability (%) of active cell is ≥90 and this means that the leucite glass-ceramics did not demonstrate a cyctotoxic effect at all concentrations under the condition of the study. Both negative and positive controls performed as anticipated. In MTT assay, the well with the highest absorbance indicates the highest cell viability.

Conclusion

The highly pure natural Malaysian silica sand can be used as SiO_2 source for producing leucite glass-ceramics without any further chemical upgrading. Sintering of SiO_2-Al_2O_3-K_2O glass powder at 700 to 850°C for duration of 1.0 to 12 h contributed to the crystallization of cubic leucite and sanidine with minor phases of microcline. The leucite glass-ceramics has a flexural strength comparable with commercial product. The absence of apatite layer on the surface indicated that it is an inert bioactive material.
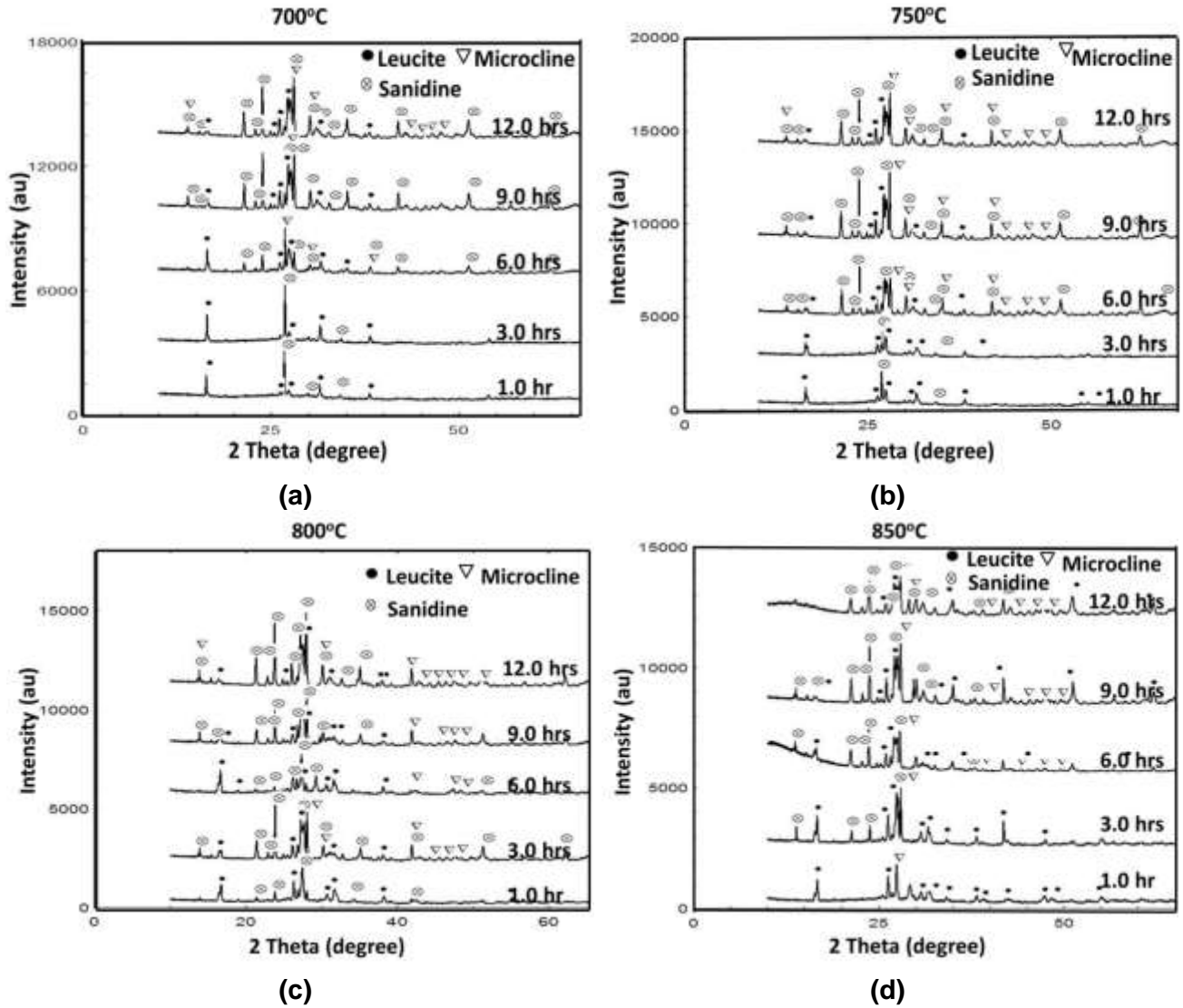
Figure 4. XRD patterns of glass-ceramics sintered at (a) 700°C (b) 750°C (c) 800°C and (d) 850°C and soaked for 1.0, 3.0, 6.0, 9.0 and 12.0 h.
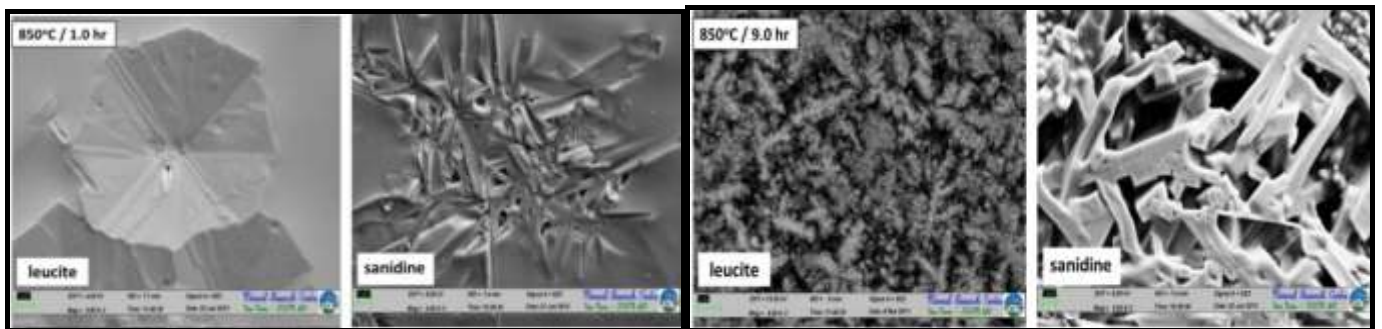
Figure 5. FESEM micrographs of glass-ceramics sintered at 850°C for 1.0 and 9.0 h.

The leucite glass-ceramics is ranked non-cytotoxic in terms of *in vitro* cellular response to human cell lines
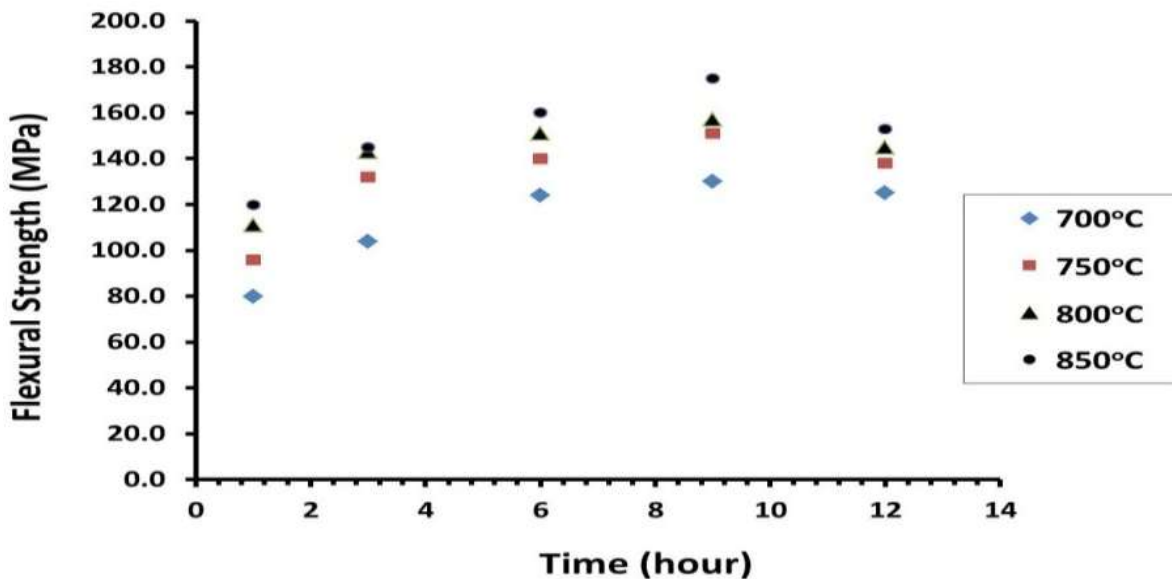
Figure 6. Flexural strength of sintered glass at 700, 750, 800 and 850°C, respectively.
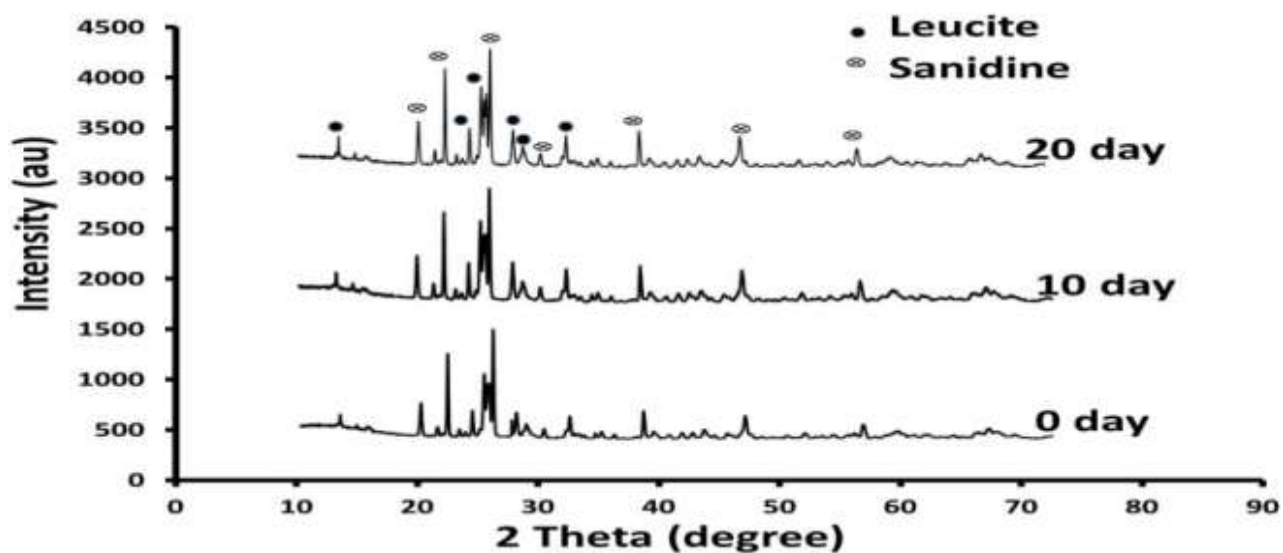
Figure 7. The XRD pattern of SBF test.

Table 2. OD values and L929 cell viability obtained after 24 h exposure to the test material and controls

	Negative control	Positive control	Leucite glass-ceramic (mg/ml)					
			6.25	12.5	25	50	100	200
	1.616	0.501	1.537	1.666	1.374	1.577	1.477	1.576
OD (570 nm)	1.674	0.551	1.698	1.583	1.622	1.523	1.586	1.355
	1.652	0.516	1.603	1.477	1.522	1.444	1.605	1.496
Mean	1.647	0.523	1.613	1.575	1.506	1.515	1.556	1.476
SD	0.03	0.03	0.08	0.09	0.12	0.07	0.07	0.11
Viability (%)	100	32	98	96	91	92	94	90
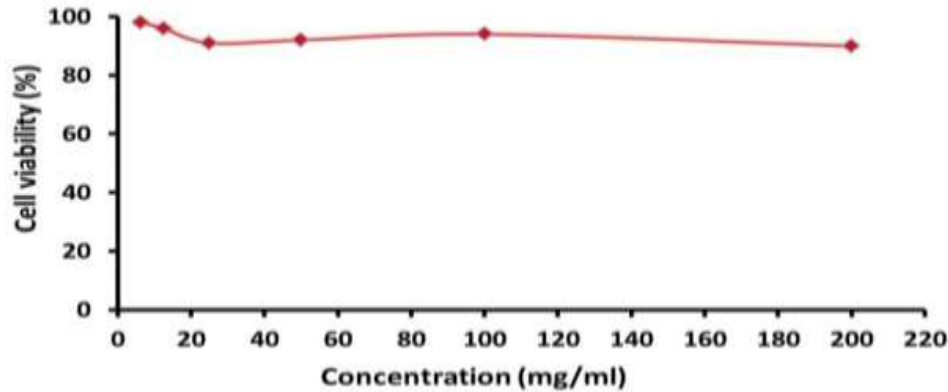
Figure 8. Viability of L929 cells at various concentrations of the test material.

under the prevailing test conditions.

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Conflict of Interests

The authors have not declared any conflict of interests.

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Full Length Research Paper

Preliminary research on strength of polymer modified concrete with copolymer natural rubber as concrete additives

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Polymer modified concrete is one of the alternative material of construction to obtain better performance in strength and durability of concrete. There are some types of PMC such as natural rubber, synthetic rubber, modified rubber and asphalt. In this work, copolymer of natural rubber styrene and copolymer of natural rubber methacrylate were used as PMC added to Portland cement concrete and Portland Pozzolan cement concrete up to 1 wt%. The aims of this work were to investigate the effects of curing methods (air curing and saturated lime curing) and addition of plasticizer on the compressive strength of concrete. Interactions among parameters were observed using factorial design analysis with Minitab (software) and strength value in concrete age of 28 days as a yield. The result showed that by saturated lime curing, calcium hydroxide as side product of cement hydration could be reacting with pozzolanic material of cement. So, there would be more calcium silicate hydrate (CSH) crystal that improve bond in the interfacial zone. It was found that the saturated lime curing produced concrete with compressive strength 20% higher than concrete produced by air curing. This result was supported by results from Scanning Electron Spectroscopy (SEM) that prove there were compactness factor of concrete structure. It was also found that plasticizer did not significantly influence compressive strength of concretes.

Key words: Polymer modified concrete, copolymer of natural rubber, strength development, saturated lime curing.

INTRODUCTION

Indonesia as a developing country had been witnessing recently a spurt in construction demand, especially for high-rise building construction. Also, In relation to the geographical condition that Indonesia is an island surrounded by the sea, located in seismic zone, so, there is a need for construction using high strength material. The concrete should provide longer service life, resist to corrosion attack due to environmental conditions and

more ductile.

Concrete used in general is Portland cement concrete or commonly known as normal concrete. The Portland cement concrete is widely used because of the physical properties and economic value. Nevertheless, there are some limitations, such as flexural strength, brittle with low failure strain, and low chemicals resistance (acids, sulfate or chloride). The limitation come from the interfacial zone, the area between the aggregate and the cement paste, giving a gap that contribute to porosity and also the differences natures between aggregates and cement paste.

The use of steel reinforcing concrete, high performance concrete, concrete protection, etc., could solve the Portland cement concrete limitations. High performance concrete is an innovation due to its special concrete properties. It is produced by involving selective materials with low w/c value (0.25 to 0.4). In addition, due to its amount of cement more than normal concrete, high performance concrete needs other additives such as plasticizers to get certain workability, high water reducer for lowering the value of w/c, hydration control to regulate the hydration process, retarder to slowing the process of setting, alkali-silica reaction (ASR) to regulating silica activity, pozzolanic materials (such as fly ash, silica fume, blast furnace slag), and others. The purpose of addition of supplementary materials is to modify the interfacial zone in order to get an impermeable and low porosity concrete. Besides its advantage, the high performance concrete raises another problem from environmental and cost overview. The high consumption of cement will be categorized as eco destructive, due to cement production process emitting carbon dioxide and consuming natural resources. Also, high performance concrete more expensive than normal concrete due to additive and admixture usage. Other limitation of high performance concrete is the brittle properties and low failure strain, which could promote water penetration, chloride penetration and chemical penetration and initiate corrosion.

In construction, there is another method of improving the service life is by corrosion prevention of reinforcement steel by cathodic protection, galvanized, plating (coating), etc. Also, increasing the concrete cover method could be used in corrosion preventing. It can be concluded that improving service life of concrete needs a complete consideration. Technical aspect, cost and environmental should be taken into account in designing concrete mixture.

Based on several reports [ACI 548.3R-03], addition of polymer could eliminate the concrete limitation. Research has been developed in several countries involving the type of polymer such as natural rubber (Muhammad et al., 2012), modified natural rubber (Sih, 2007; Ariyadi et al., 2010), synthetic rubber, Styrene Butadiene Rubber (João, 2009; Pacheco and Jalali, 2009), epoxy (Elalaoui et al., 2012), poly vinyl, acrylic, poly vinyl acetate,

asphalt, tar, paraffin, and others. The polymer addition into concrete mixture could improve strength and durability. So, it can widen the concrete application. The addition of polymer is one of the alternatives to get high performance concrete [www.ce.memphis.edu]. The purpose of polymer addition is manipulating the interfacial zone, which is the weakest point of the concrete, and filling the concrete void that could serve as corrosive material entry point.

The polymer strengthening mechanism in concrete is processed during cement hydration and polymer incorporation. While hydration reaction occurs, the concrete mixture begins to setting and hardening, polymer molecules begin to concentrate in void area [ACI 548.3R-03]. Besides water removal due to cement hydration process, evaporation, and their combination, the polymer particles coalesce either forming a film on calcium silica hydrate (CSH) or co-matrix that interweave the aggregate particles. So, there will be small interstices, resulting concrete more impermeable, low permeability and improving durability of seawater intrusion, abrasion and chemical resistance. By manipulating the interfacial zone and void of concrete, the addition of polymer into the concrete could improve the mechanical properties such as compressive strength, tensile strength and flexural strength.

Polymer in concrete can act as binder like cement. It can be single binder as polymer concrete, or together with cement as polymer modified concrete (Wahby, 2003). This preliminary research working with polymer as additional binder with cement in polymer modified concrete development.

In 2014, Indonesia is the largest natural rubber production in the world. Most rubbers are exported as raw material. In order to get added value of rubber, research on rubber modification had been done using styrene and methacrylate (Marga, 2007). The modification purposes aim to get harder and stronger rubber as styrene butadiene rubber and methyl methacrylate rubber properties.

There are some influencing factors in polymer modified concrete strength development. They are cement type, curing method, interaction with plasticizer, polymer type, polymer concentration, etc. The preliminary research in polymer modified concrete using natural rubber involved cement type (Portland cement and Portland pozolan cement), curing method (saturated lime curing and air curing), using plasticizer (with and without plasticizer), and type of polymer (natural rubber styrene copolymer and natural rubber methacrylate rubber copolymer). Cements used for concrete mixture were Portland cement and Portland Pozzolan cement. The variation of cements based on Indonesian cements industries is trendy. In Indonesia, Portland cement production had been reduced in order to be more environmentally friendly, and commitment of Indonesia for Kyoto protocol in reducing carbon dioxide emission. So, Portland Pozzolan cement

is an alternative in cement industries. Its production of reducing clinker content is replaced by pozzolanic material (natural pozzolanic sand/trass). The polymers used natural rubber styrene copolymer and natural rubber methacrylate copolymer. They were produced either from copolymerization reaction between natural rubber and styrene or natural rubber and methacrylate. The copolymerization is done using Gamma rays reactor. These copolymers were researched by Natural Nuclear Energy Agency (BATAN-Indonesia).

Analysis of using two factors factorial design two levels was made for determining significant effect among those factors and concrete strength of 28 days of age will be defined as yield (Box et al., 2005). The purpose of this preliminary research was to determine the significant factor among cement type, curing method, using of plasticizer and type of polymer which could give either high quality concrete or high performance concrete. This preliminary research will be used as database for research.

EXPERIMENTAL

Material

Concrete was prepared using local material at Indonesia. The materials had been characterized suitably with Indonesian National standards (SNI). The cements were characterized using SNI 15-2049-2004 Semen Portland (Portland Cement) and SNI 15-0302-2004 Semen Portland Pozolan (Portland Pozzolan Cement). And aggregates were characterized using Indonesian National Standards that were adopted from ASTM C 33/C 33 M-11 (2011), Standard Specification for Concrete Aggregates. The standards are SNI 1969:2008 Cara uji berat jenis dan penyerapan air agregat kasar (Testing Method for density and water absorption of coarse aggregates), SNI 1970:2008 Cara uji berat jenis dan penyerapan air agregat halus (Testing Method for density and water absorption of fine aggregates), SNI 2417:2008 Cara uji keausan agregat dengan mesin abrasi Los Angeles (Testing Method for abrasion resistance of coarse aggregates in Los Angeles Machine), and others. The aggregates were washed to remove clay and organic materials.

The qualities of cements (chemical and physical properties) are shown in Tables 1 and 2, respectively. The physical properties of these cements are quite similar. Portland Pozolan cement is produced by reducing the clinker content and substituting with natural pozzolanic material about 25%.

Natural rubber styrene copolymer (KOLAS) and natural rubber methacrylate copolymer (KOLAM) are characterized using ASTM D 1076-10. Between them, KOLAS give dry rubber and total dissolved solid slightly higher than KOLAM. Also, KOLAS is more viscous than KOLAM. The quality of KOLAS and KOLAM are shown in Table 3.

Sample preparation

Concrete samples were prepared as per National Indonesian Standard (SNI) 7656:2012 Tata Cara Pemilihan beton normal, beton berat dan beton massa. The standard is adopted with some modification from ACI 211.1-91 Standard Practice for Selecting Proportion for normal, heavy weight, and mass concrete. Table 4 shows the concrete mix design and its composition of aggregate, cement and water. The composition of polymer is 1% weight/weight of cement.

The cement and aggregate (dry mix) were mixed using concrete mixture for 1 min. The polymer was mixed with water separately and they mix together with dry mix for 2 min. Superplasticizer used in mixture, was added in 1 last minute. And the total time of mixing would be 3 or 4 min (Figure 1; Sequence of sample preparation).

FACTORIAL DESIGN AT TWO LEVELS

The factorial design at two level designs was chosen in determining significant effect and interaction among research parameters. This preliminary research involving 4 parameters, so, based on factorial design at two level they will be 16 (2^4) yields. The research parameters were type of cements, type of polymers, curing method and addition of plasticizer. The research yield was concrete strength of 28 days that analysed using ASTM (ASTM C 39/C 39 M-04a (2004), Standard Test Method for Compressive strength of Cylindrical Concrete Specimen). Table 5 shows the combination of parameters and yields. The data are plotted into normal plot (Figure 2) and each interaction for each parameter is plotted into main effect response plot curve (Figure 3). The analysis of continuing among parameters into interaction plot for response is as shown in Figure 4.

Based on Figure 2, the significant effect were cement type and curing method. In this preliminary research, cement type will be omitted. By considering the purposes of this research will be optimizing Portland Pozzolan cement in polymer modified concrete application, to be environmental friendly concrete; so, this preliminary research, cement type effect will be omitted. The research will be more detail in curing method. The data shown are polymer modified concrete with Portland Pozzolan cement. During 28 days, concretes were cured in saturated lime submersion (saturated lime curing method) and on temperature room (air curing method). Saturated lime method was chosen because of Portland Pozzolan cement usage. The Portland Pozzolan cement replaces about 15 to 35% clinker by pozzolanic materials.

Thus, the pozzolanic material would react with calcium

Table 1. Chemical and physical properties of Portland cement.

Description	Testing result	Unit	Requirement based on SNI 15-2049-2004
Chemical composition			
1 Insoluble residue	1.57 ± 0.06	%	Max. 3.0
2 Silicon dioxide, SiO_2	19.57 ± 0.21	%	-
3 Iron (III) oxide, Fe_2O_3	3.60 ± 0.09	%	-
4 Alumunium oxide, Al_2O_3	6.52 ± 0.25	%	-
5 calcium oxide, CaO	63.20 ± 0.15	%	-
6 Magnesium oxide, MgO	1.14 ± 0.05	%	Max. 6.0
Sulfur Trioxide, SO_3			
7 C3A < 8.0%	-		
C3A > 8.0%	2.02 ± 0.08	%	Max. 3.5
8 Loss of ignition	4.14 ± 0.05	%	Max. 5.0
9 Alkali as Na_2O	0.52 ± 0.04	%	Max. 0.6
10 Free lime	1.46 ± 0.12	%	-
C3S	47.9		-
C2S	20.0		-
C3A	11.2		-
C4AF	10.9		-
Physical properties			
1 Fineness as Blaine	329	m^2/kg	Min. 280
Setting time (Vicat)			
2 Initial	170	min	Min. 45
Final	225	min	Max. 375
Autoclave expansion			
3 Expansion	0.02	%	Max. 0.8
Shrinkage	-	%	Max. 0.2
Compressive strength			
4 3 days	190	Kg/cm^2	Min. 125
7 days	259	Kg/cm^2	Min. 200
28 days	349	Kg/cm^2	Min. 280
False set			
5 Final penetration	87	%	Min. 50
6 Air content (mortar)	5.8	% (v/v)	Max. 12
7 Spesific gravity	3.03	g/ml	

Table 2. Chemical and physical properties of Portland Pozolan cement.

Description	Testing result	Unit	Requirement based on SNI 15-0302-2004
Chemical composition			
1 Insoluble residue	13.33 ± 0.06	%	
2 Silicon dioxide, SiO_2	27.81 ± 0.21	%	
3 Iron (III) oxide, Fe_2O_3	3.95 ± 0.09	%	

Table 2. Contd.

4	Alumunium oxide, Al_2O_3	7.93 ± 0.25	%	
5	calcium oxide, CaO	52.85 ± 0.15	%	
6	Magnesium oxide, MgO	1.23 ± 0.05	%	Max. 6.0
7	Sulfur Trioxide, SO3	2.88 ± 0.10	%	Max. 4.0
8	Loss of ignition	2.69 ± 0.05	%	Max. 5.0
9	Alkali as Na_2O	0.48 ± 0.04	%	
10	Free lime	0.92 ± 0.09	%	

Physical properties

1	Fineness as Blaine	371	m^2/kg	Min. 280
	Setting time (Vicat)			
2	Initial	170	mine	Min. 45
	Final	255	min	Max. 375
	Autoclave expansion			
3	Expansion	0.02	%	Max. 0.8
	Shrinkage	-	%	Max. 0.2
	Compressive strength			
4	3 days	184	kg/cm^2	Min. 125
	7 days	251	kg/cm^2	Min. 200
	28 days	357	kg/cm^2	Min. 250
5	**False set**			
	Final penetration	74	%	Min. 50
6	Air content (mortar)	5.8	% (v/v)	Max. 12
7	Spesific gravity	3.03	g/ml	

Table 3. Polymer properties (tested using ASTM D 1076-10).

S/No	Parameter	Unit	KOLAS	KOLAM
1	Total alkali as ammonia	%	0.20	0.14
2	Dry rubber content	%	43.85	38.10
3	Solid content	%	45.47	40.30
4	Coagulum content	%	0.0003	0.0031
5	pH	NA	9.59	8.48
6	sludge content		2.77	0.002
7	Density	g/ml	0.98624	0.99589
8	Viscosity	Cp	13.4	11.1
9	Magnesium ion	%	0	0

KOLAS = Natural rubber styrene copolymer; KOLAM = Natural rubber methacrylate copolymer.

hydroxide $(Ca(OH)_2)$, by product of cement hydration, resulting in another calcium silicate hydrate. There is an additional pozzolanic reaction in concrete. The saturated lime curing method gave stronger concrete than air curing method. There were variation and the maximum differences of about 20% between 2 curing methods (Figure 5). It is supported by microstructure analysis.

The microstructure of concrete showed that saturated

Table 4. Concrete mix design.

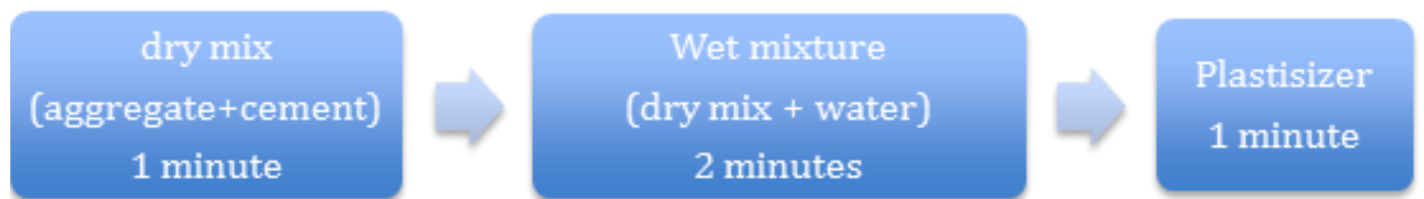| S/No	Parameter	Calculation	Value	Remarks
	Strength (Fc)	Definitive	40	Mpa
1	Safety factor	Definitive	4.1	MPa
	Fc'	Fc + safety factor (fc+1.64 SF)	44.1	
2	Cement tpe	Definitive	Portland cement and Portland pozolan cement	
3	Coarse aggregate	Definitive	Crushed stone	
	Fine aggregate	Definitive	sand	
4	Workability	5.3.1.1 Table1	75 – 100 mm	SNI 7656:2012
5	Size aggregate, maks	5.3.1.2	20 mm	SNI 7656:2012
6	Water content	Table 2	205	SNI 7656:2012, kg/cm^3
7	Water/cement (w/c)	Pasal 5.3.1.4 tabel 3 dan 4	0.379	
8	Cement content	(6/7)	540.897	kg/cm^3
9	Coarse aggregate	5.3.1.4 Table 3	0.61	SNI 7656:2012
		Dry weight = 1430 kg/m^3	872.3	kg/cm^3
10	Concrete density	Table 6	2345	kg/cm^3
10.1	Weight of fine aggregate	10-6-8-9	726.803	kg/cm^3
10.2	Composition based on volume absolute			
	a. Water	=6:1000	0.205	m^3
	b. Cement	= 8 : (3.15 × 1000)	0.172	m^3
	c. Coarse aggregate	= 9 : (Bj SSD × 1000)	0.338	m^3
	d. Air entrainment	=1% × 1	0.01	m^3
	e. Fine aggregate	= 1.0 – (a + b + c +d)	0.275	m^3
	f. Fine aggregate volume	= e	0.275	m^3
	g. fine aggregate in dry basis	= e × Bj SSD × 1000	721.875	kg
Composition		Weight basis, kg/m^3	Volume estimation, kg/m^3	
Water		205	205	
Cement		540	540	
Fine aggregate		726	721	
Coarse aggregate		872.3	872.3	

**Figure 1.** Sequence of sample preparation.

lime could modify the interfacial zone to be more impermeable and compact (Figures 6 and 7). In Figure 6, the interfacial zone of polymer modified concrete is compact among aggregates, cement paste and polymer films. This condition expected could improve either strength or durability.

In Figure 4, it could be observed that saturated lime curing method is highly effective in strengthening of

Table 5. Research design and yield.

S/No	Cement type	Polymer type	Curing method	Plasticizer addition	Yield (strength 28 days)
1	Portland Pozzolan	KOLAM	Saturated lime	Plasticizer	37.76
2	Portland type I	KOLAM	Saturated lime	Plasticizer	40.03
3	Portland Pozzolan	KOLAS	Saturated lime	Plasticizer	29.57
4	Portland type I	KOLAS	Saturated lime	Plasticizer	41.46
5	Portland Pozzolan	KOLAM	Air curing	Plasticizer	31.79
6	Portland type I	KOLAM	Air curing	Plasticizer	34.05
7	Portland Pozzolan	KOLAS	Air curing	Plasticizer	26.37
8	Portland type I	KOLAS	Air curing	Plasticizer	36.19
9	Portland Pozzolan	KOLAM	Saturated lime	-	36.04
10	Portland type I	KOLAM	Saturated lime	-	44.55
11	Portland Pozzolan	KOLAS	Saturated lime	-	34.92
12	Portland type I	KOLAS	Saturated lime	-	40.07
13	Portland Pozzolan	KOLAM	Air curing	-	31.74
14	Portland type I	KOLAM	Air curing	-	35.26
15	Portland Pozzolan	KOLAS	Air curing	-	32.16
16	Portland type I	KOLAS	Air curing	-	34.89

Lenth's PSE = 1.29
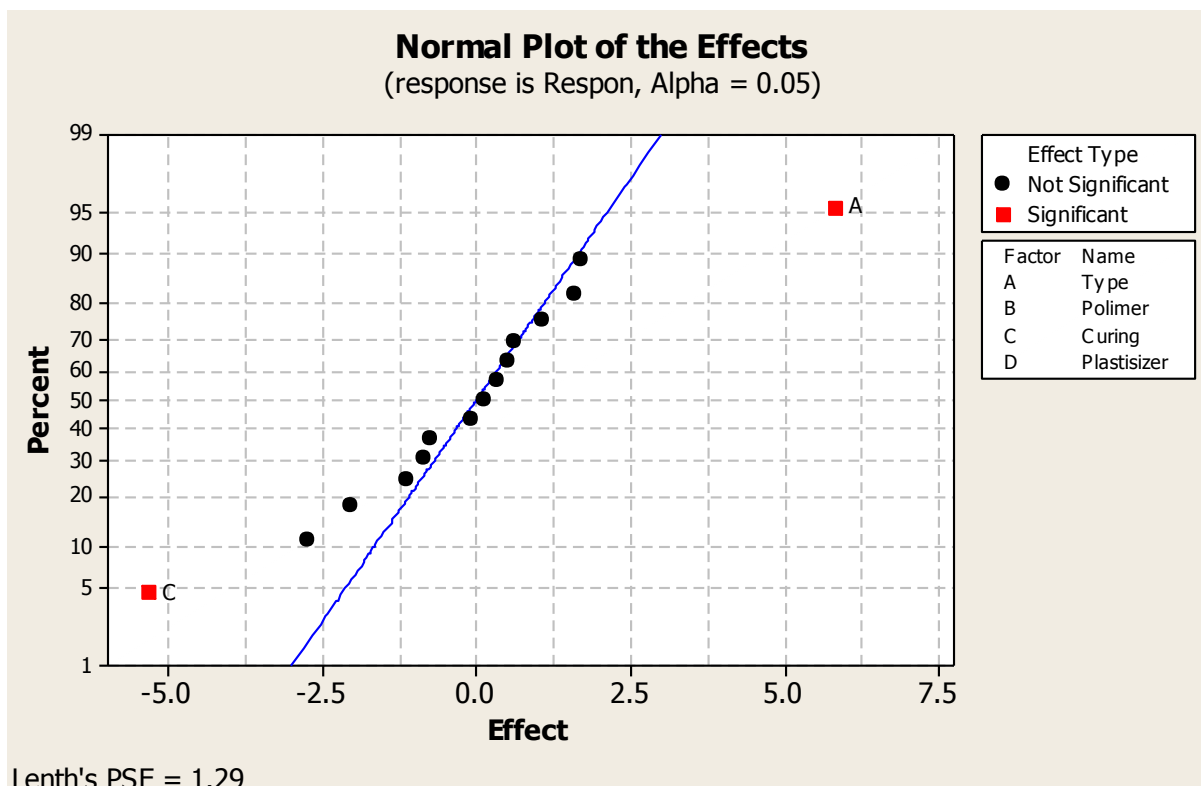
Figure 2. Normat plot.

concrete, either for Portland cement or Portland Pozzolan cement, and KOLAM or KOLAS as concrete additives. The work of plasticizer in concrete was not significant, either for normal concrete or polymer modified concrete.

So, there was no negative interaction between polymer and plasticizer when used together in concrete. It would be an advantage when concrete workability is low (high concentration of polymer used).
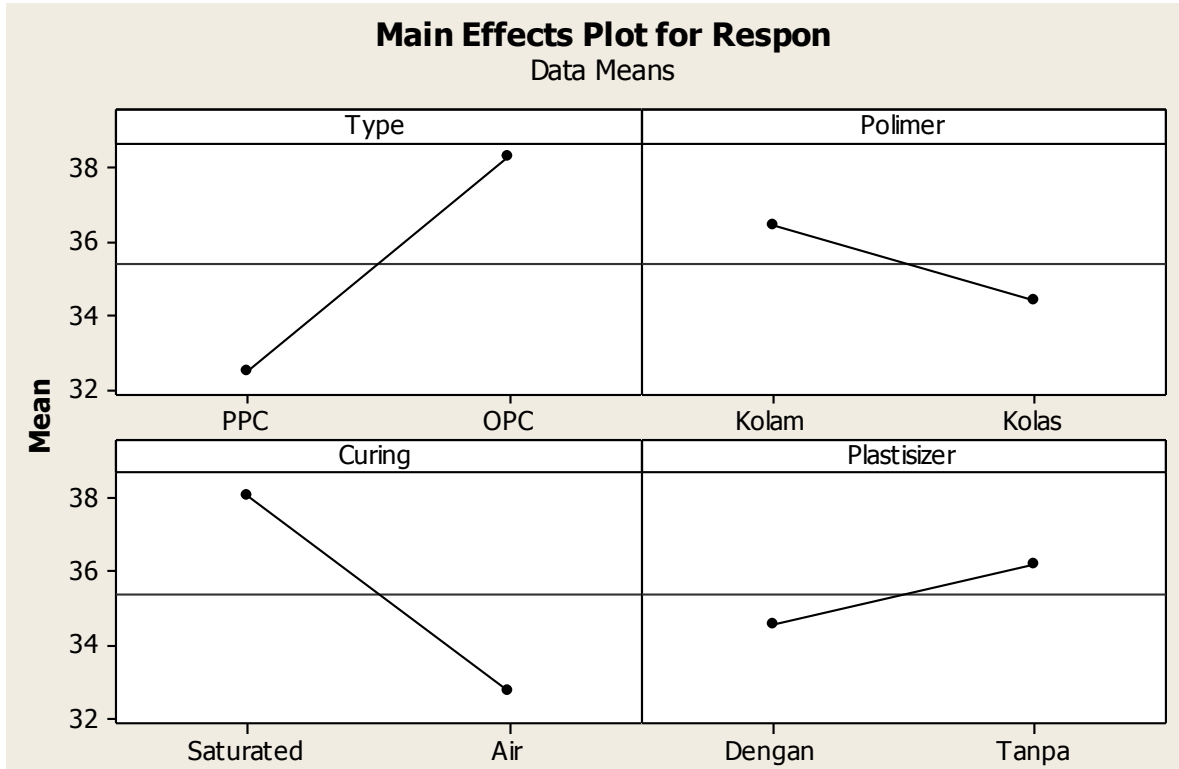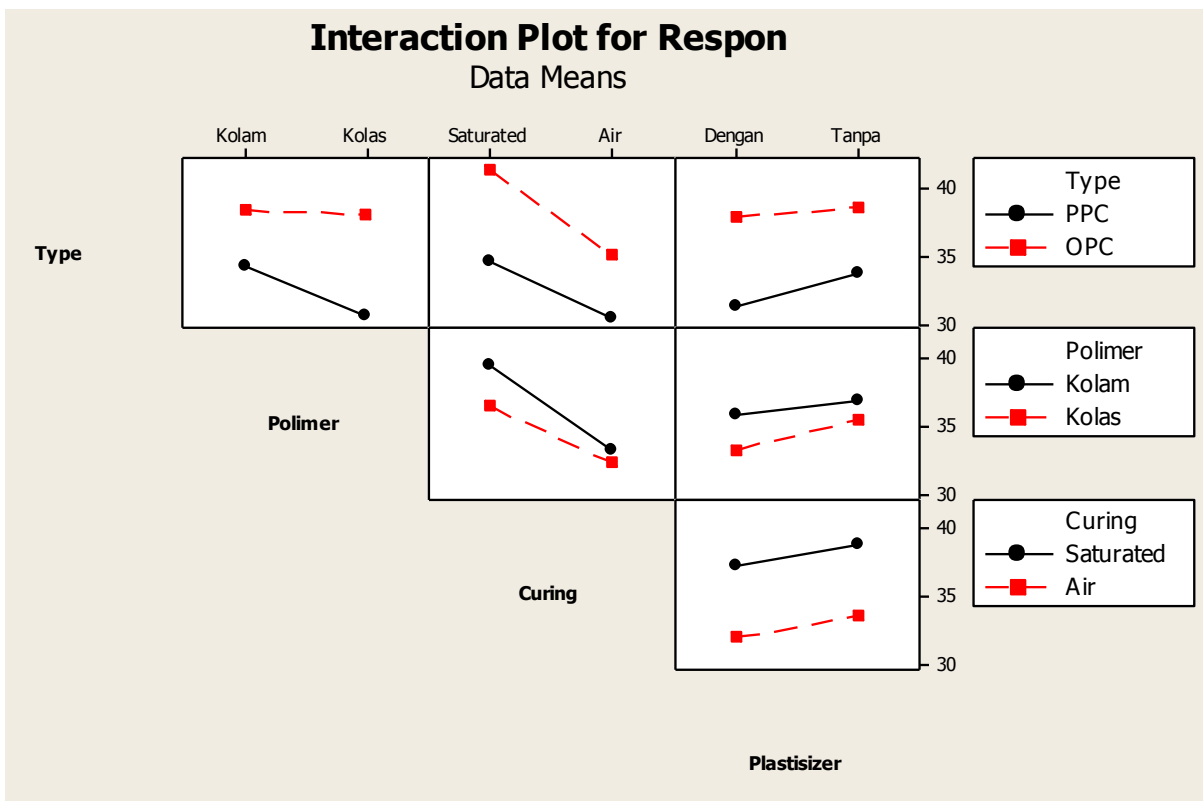
Figure 3. Main effect.
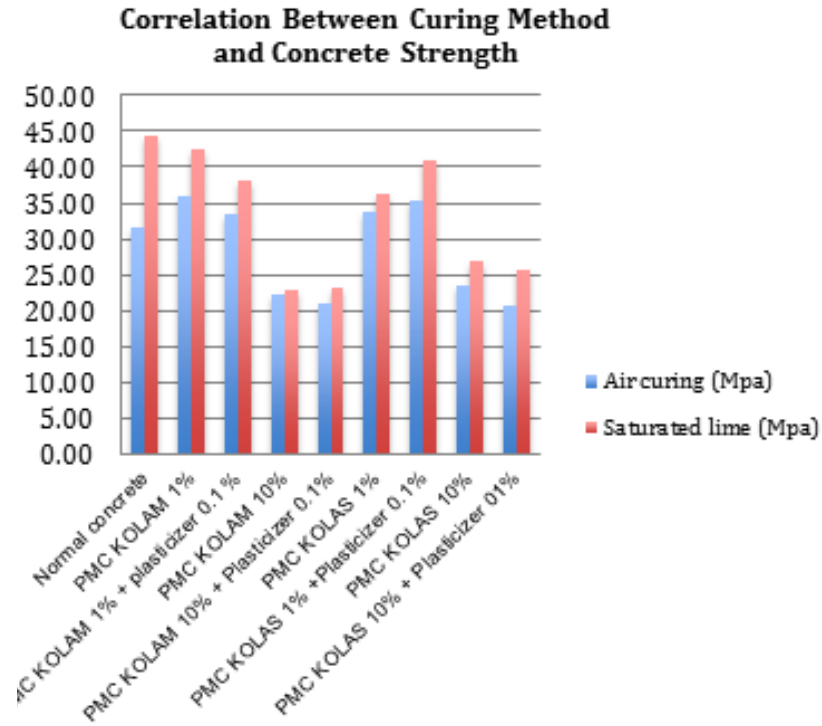

Figure 4. Interaction among factor.

Figure 5. Correlation Between curing method and concrete strength.
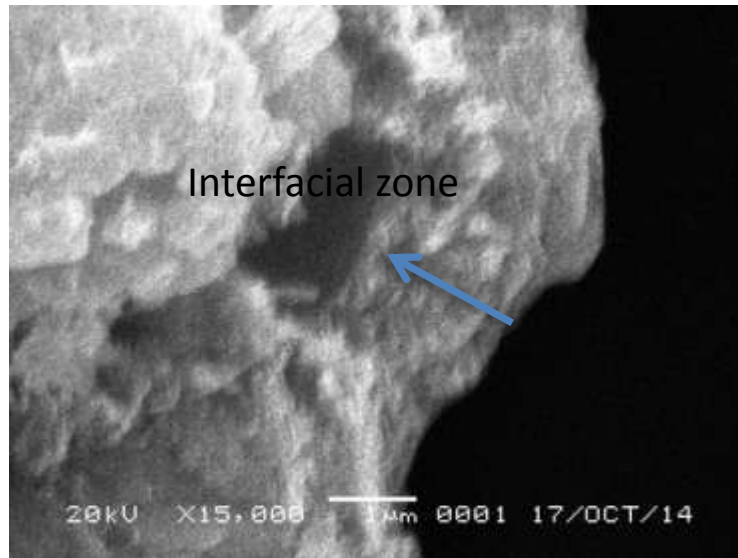

Figure 6. Microstructure of polymer modified concrete.

Conclusion

The strength of polymer modified concrete is affected by several factors; with significant effect which is the curing method. The saturated lime curing method, gives higher concrete strength of 20% maximum than air curing.

There is no significant difference of concrete strength between KOLAS and KOLAM; in addition, there is 10% difference. The usage of plasticizer will not affect the concrete strength, while mixed with polymer.

The strength of polymer modified concrete will be optimum by saturated lime curing method with KOLAS as
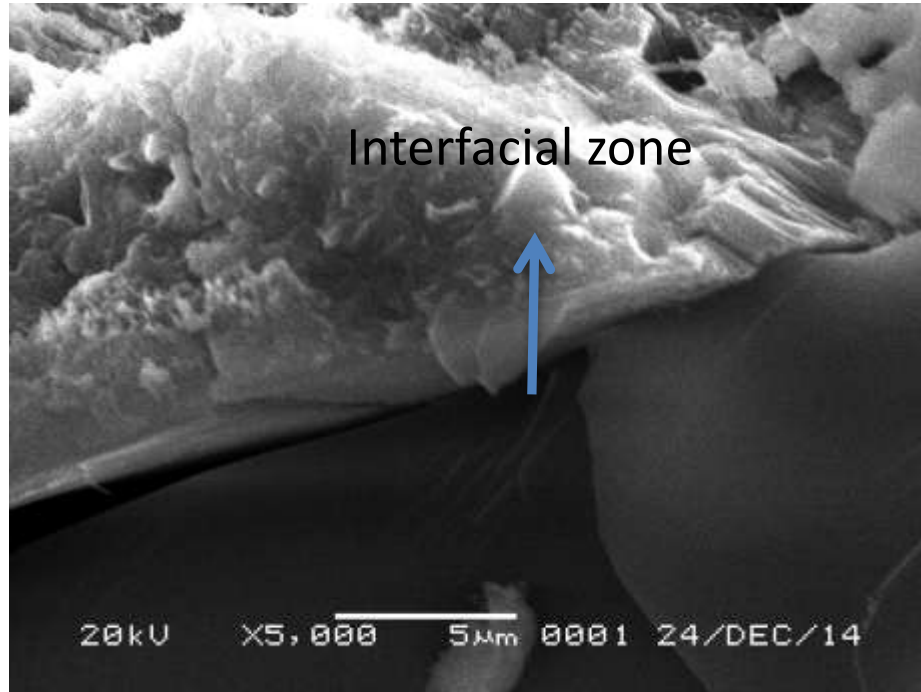
Figure 7. Microstructure of normal concrete.

polymer either with or without plasticizer, for polymer concentration up to 1% weight of cement.

Conflict of Interests

The authors have not declared any conflict of interests.

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