UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF GLASS POLYALKENOATE CEMENT WITH MODIFIED MONTMORILLONITE

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By

NUR'IZZAH BINTI MD NASIR

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PREPARATION AND CHARACTERIZATION OF GLASS POLYALKENOATE CEMENT WITH MODIFIED MONTMORILLONITE

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Chairman : Norhazlin Zainuddin, PhD
Faculty : Science

Glass polyalkenoate cement (GPC) is a water based cement which is formed by acid base reaction with poly(acid) and aluminosilicate glass. Glasses with vary amount of phosphate were prepared with compositions $4.5SiO_2$-$3Al_2O_3$-$2CaF_2$-$3CaO$-xP_2O_5, where x=0, 0.75, 1.5, 3, and 4.5 using the hot melting technique. Sodium montmorillonite (Na-MMT) was modified into cationic (Mg, Al, Ca) and organo MMTs (12-aminoddodecanoic acid, ADA and octadeylamine, ODA). Selected MMTs were introduced to the GPC formulation and the setting reaction of the GPCs was studied using the FTIR spectroscopy. Cements were divided into GPC, GPC with addition of Na-MMT, and GPC with addition of modified Na-MMT (GPC+ODA-MMT/GPC+Al-MMT). The XRD patterns of all glasses showed amorphous phase except for IU45 glass (x=4.5 mole P_2O_5). XRD pattern for IU45 glass showed few sharp crystalline peaks, which is well-matched with $AlPO_4$. ^{27}Al MAS-NMR for all glasses except IU45 glass showed only the present of aluminium ions in 4- fold coordination with oxygen. While, for IU45 glass showed the aluminium ions present in 4- and 6- fold coordination with oxygen, which corresponded to the presence of $AlPO_4$. FTIR spectrum for IU45 glass showed strong band at the 1080 - 1110 cm^{-1} region, which corresponded to the P–O stretch of the structural PO_4 groups. Combination of XRD, MAS-NMR and FTIR results showed that the crystal in IU45 glass was $AlPO_4$. For the cement part, FTIR spectrum showed the shoulder band at 950 cm^{-1} may be due to the formation of hydrated silica gel (Si-O(H) stretch) and the new band at 1560 cm^{-1} corresponded to the cross linking band (COO^-M^+). The shoulder band can only be observed in the earlier reaction of GPC and disappeared with time. Cross linking reaction caused the bending vibrations of C-H_2 and CH-C=O at 1440 cm^{-1} and 1415 cm^{-1}, respectively were slightly shifted to higher wave number. The carboxylic acid peak for GPC+Al-MMT disappeared slightly faster compared with GPC+ODA-MMT, GPC and GPC+Na-MMT. In compressive strength test, GPC+ODA-MMT and GPC+Al-MMT gave highest strength (75 – 85 MPa) at the beginning of setting reaction while GPC+Na-MMT gave the lowest strength (45.5 MPa). However, the strength of GPC+Na-MMT increased rapidly after 1 day aging time and kept increasing until 28 days. This study

suggested that GPC+Al-MMT was slightly sped up the setting reaction while GPC+modified Na-MMT increased the compressive strength at early stage of the GPC setting reaction.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah (Sarjana Sains)

PENYEDIAAN DAN PENCIRIAN SIMEN KACA POLIALKENOAT DENGAN MONTMORILONIT TERUBAHSUAI

Oleh

NUR' IZZAH BINTI MD NASIR

April 2014

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Simen kaca polialkenoat (GPC) adalah simen berasaskan air yang terhasil daripada tindak balas asid bes dengan poli(asid) dan kaca aluminosilikat. Kaca dengan perbezaan kandungan fosfat disediakan dengan komposisi kaca $4.5SiO_2$-$3Al_2O_3$-$2CaF_2$-$3CaO$-xP_2O_5, di mana x=0, 0.75, 1.5, 3, dan 4.5 dengan meggunakan teknik panas lebur. Sodium montmorilonit (Na-MMT) telah diubahsuai kepada kationik (Mg, Al, dan Ca) dan organo – MMT (asid 12-aminododekanoik, ADA dan oktadesilamina, ODA). Na-MMT terubahsuai yang terpilih telah diperkenalkan dalam pembentukan simen dan aturan tindak balas dalam GPC dikaji menggunakan spektroskopi FTIR. Simen telah dibahagikan kepada GPC, GPC dengan penambahan Na-MMT, dan GPC dengan penambahan Na-MMT terubahsuai (GPC+ODA-MMT dan GPC+Al-MMT). Corak XRD untuk semua kaca menunjukkan fasa amorfus kecuali kaca IU45 (x=4.5 mol P2O5). Corak XRD pada kaca IU45 menunjukkan beberapa puncak hablur yang sepadan dengan $AlPO_4$. ^{27}Al MAS NMR bagi semua kaca kecuali kaca IU45 menunjukkan hanya kewujudan ion aluminium dalam 4- koordinasi dengan oksigen. Manakala, bagi kaca IU45 menunjukkan ion aluminium wujud dalam 4- dan 6- koordinasi dengan oksigen yang sepadan dengan kehadiran $AlPO_4$. Spektrum FTIR untuk kaca IU45 menunjukkan puncak kuat di antara 1080-1110 cm^{-1} yang sepadan dengan P-O (regang) bagi struktur kumpulan PO_4. Gabungan keputusan XRD, MAS-NMR, dan FTIR menunjukkan bahawa hablur dalam kaca IU45 adalah $AlPO_4$. Untuk bahagian simen, spektrum FTIR menunjukkan puncak bahu pada 950 cm^{-1} berkemungkinan merujuk kepada pembentukan gel silika hidrat (Si-O(H) dan punca baru yang muncul pada nombor gelombang 1560 cm^{-1} merujuk kepada puncak rangkai silang (COO^-M^+). Puncak bahu bagi gel silika hidrat hanya dapat diperhatikan pada awal tindak balas GPC dan hilang dengan penambahan masa. Tindak balas rangkai silang telah menyebabkan getaran lenturan bagi C-H_2 dan CH-C=O pada nombor gelombang 1440 cm^{-1} dan 1415 cm^{-1} sedikit beralih kepada nombor gelombang yang lebih tinggi. Puncak asid karbosilik bagi GPC+Al-MMT menghilang sedikit cepat berbanding dengan GPC+ODA-MMT, GPC, dan GPC+Na-MMT. Untuk kekuatan mampatan, GPC+ODA-MMT dan GPC+Al-MMT memberi kekuatan yang paling tinggi berbanding simen yang lain di permulaan aturan tindak balas, manakala GPC+Na-MMT memberi kekuatan

paling rendah. Namun, selepas 1 hari aturan, kekuatan GPC+Na-MMT meningkat dengan mendadak dan terus meningkat hingga hari ke 28. Di dalam kajian ini, GPC+Al-MMT meningkatkan sedikit kadar tindak balas manakala GPC+Na-MMT terubahsuai meningkatkan kekuatan mampatan pada peringkat awal aturan tindak balas GPC.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisor Committee were as follows:

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LIST OF ABBREVIATION

ATR	Attenuated total reflectance
BO	Bridging oxygen
d_{001}	d spacing
FTIR	Fourier transform infrared
GPC	Glass polyalkenoate cement
ICP	Inductive conductivity plasma
MAS-NMR	Magic-angle spinning nuclear magnetic resonance
MMT	Montmorillonite
M_w	Molecular weight
NBO	Non bridging oxygen
PAA	Polyacrylic acid
PTFE	Polytetrafluoroethylene
XRD	x-ray diffraction

CHAPTER 1
INTRODUCTION

1.1 Background

Glass polyalkenoate cement, GPC is water based cement which is formed by the acid base reaction between aqueous polyacid and fluroaluminosilicate glass. The reaction releasing ion such as Al^{3+}, F^{-}, Ca^{2+} for polyacid linking with the surface of the aluminosilicate glass (Nicholson, 1998). Hydrolysis reaction takes place on the surface of glass, where the polyacid in the presence of water attacks the glass network, which causes the leaching of metal cations such as Al^{3+}, Ca^{2+} and F^{-} from the glass. These metal cations then ionically cross link with polyacid chain to form polysalt matrix resulting hard ceramic-like cement. While, the surface of the glass developed into silica gel layer, $Si(OH)_4$.

GPC is a great candidate to replace the function of amalgam as it has ability to chemically bond to the tooth structure, biocompatible, low shrinkage and can release fluoride to protect the tooth from secondary caries. Although amalgam is successfully as a universal tooth filling material for over century, controversy still exists mainly because of the presence of mercury in amalgam. Other than that, amalgam also able to tarnish the tooth applied and can form micro-leakage on the tooth.

Almost 20 years study had been done toward the GPCs for it's to become the same level as the amalgam. Various fillers have been applied to conventional glass polyalkenoate restoratives to improve their mechanical properties and enable posterior use clinically, including alumina-silicate (Kobayashi et al., 2000), fused fibre (Ruddell et al., 2002), hydroxyapatite (Lucas et al., 2003), zirconia (Gu et al., 2005) and montmorillonite clay (MMT) (Dowling et al., 2006).

MMT is trilayer smectice clay consisting of stacked platelets constructed of an alumina octahedral layer sandwiched between two silica tetrahedral layers. MMT clay is easy to obtain and modified. MMT can be modified by ion-exchanging organic cationic surfactants (intercalants). The presence of Al, Si, H, and O ions in the MMT structure made it favorable to be used as filler in dental cement. MMT is a special material which has been applied widely such as filler in polymer nylon 6 by fornes by Dowling *et al.*, (2006), treatment in waste water by Zhu *et al.*, (2011) and absorbent of benzene derivative by Zhou *et al.*, (2007), Boutahala *et al.*, (2011) and Moaaz *et al.*, (2011).

In this study, the preparation and characterization of the modified MMT, aluminosilicate glass, and the GPC would be done. While, the setting reaction of GPC with addition of MMTs would be followed by using Fourier Transform Infrared (FT-IR) spectroscopy and the compressive strength of the GPC with addition of modified MMTs would be determined. In addition, the release of

aluminium ion from the GPC+MMT would be identified through Inductive Couple Plasma (ICP) analysis.

1.2 Problem statement

The modifications on the GPC in order to improve the mechanical properties were widely done previously. However, no one had repeated or improved the work done by Dowling and his co worker (2006, 2007). Dowling had used organo MMT as filler in GPC application and the study only focus on the compressive strength, working characteristic, volumetric wear and wear depth. No study had been done on the setting reaction of the GPC with addition of modified MMT, as well as the releasing of toxic element such as aluminium ion. In addition, Dowling *et al.* (2006, 2007) used commercial glass which might make the study on the setting reaction of the GPC hardly to explain. Therefore, in this study, the glass that we used was experimentally synthesized in our laboratory. Furthermore, we applied larger d spacing of MMT compared to the modified MMT used by Dowling *et al.* to study the effect of MMT's d spacing on the mechanical properties of GPC. The hypothesis proposed in this study was that MMT reinforcement would improve the compressive strength and influence the setting reaction of the GPCs.

1.3 Significance of the study

The application of GPC was widely used in medical field such as adhesive in otology and tooth cementation (Wilson and McLean, 1988), in orthopaedic surgery (Wilson and Prosser, 1962), bone cementation (Geyer and Helms, 1993), crown (Sasanaluckit et al., 1993) and recently . The capacity of GPC to chemically bond to the apatite mineral phase of tooth and the ability to release fluoride ion, which is believed to inhibit secondary caries of tooth gives the advantages for dental restorative application (De Barra and Hill, 1998; Pereira et al., 1998). Although amalgam is successfully used as an universal tooth filling material for over century, much controversy still exists mainly because it contain mercury. Other than that, amalgam also able to tarnish the tooth applied and can form micro leakage on the tooth (Meiers and Turner, 1998). However, GPCs have inferior fracture toughness and wear resistance compared to amalgam and composite resins and therefore have limited application as posterior filling materials for class I and II cavities (Lewis, 1989; Douglas and Lin, 1993). Their fracture toughness is also low for use as orthopaedic bone cements and in bonding orthodontic brackets to teeth (Akinmade and Hill, 1991). GPCs have also insufficient strength for use in high load bearing regions (Xie et al., 2000).

Montmorillonite (MMT) clay have been shown improvement in the mechanical properties of nylon 6 (Fornes and Paul, 2003) and acrylic (Biasci et al., 1994). MMT clay were applied in other field such as absorbent for phenol (Zhou et al., 2007), sorption of toluene (Moaaz et al., 2011) and treatment in waste water (Zhu et al., 2011). Dowling *et al.* (2006) had reported by using MMT as filler in

GPC, it able to increase the mechanical properties of the GPC but the influence of MMT on the setting reaction of the GPC was not mentioned clearly.

This study focussed on 3 main parts, which were glass formation, modification of Na-MMT clays, and the synthesis of glass polyalkenoate cement (with and without addition of MMT). The effects of phosphate in formation of glass network, compressive fracture strength and setting reaction of GPC with addition of MMT were studied to provide an indication of their potential use for posterior and luting dental restorative.

1.4 Objectives of the study

The aim of this study was to characterize the glass and MMTs structure, and GPCs by using X-ray diffraction, inductive couple plasma (ICP), Fourier Transform Infrared (FTIR), and mean compressive strength in order to:

1. investigate the effect of phosphorus content in glass network using XRD and MAS-NMR.
2. study the compressive strength of the GPC with and without addition of montmorillonite.
3. determine the setting reaction of GPC by using FTIR.

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