Summary and Conclusion

CHARACTERIZATION OF THE BIO-ACTIVE GLASSES THROUGH ULTRASONIC STUDIES

Introduction

The development and application of new engineering materials have provided the technological support for the spectrum of needs such as high frequency transistors, data storage devices, display screens, aeronautical materials, anti-corrosive materials, biological applications etc. The fabrication of highly compatible materials which should withstand in various physical and chemical parameters are essentially required. The identification and selection of a suitable material for the particular application in the field of material science leads to the success of the technological transfer. In biomaterials, three different types of materials viz. first, second and third generations of biomaterials have been developed. In earlier days, relatively few engineering materials such as stainless steel, chromium steel etc. were used to make artificial parts of relatively simple design. Today the field of biomaterials has evolved to such an extent for different biomedical applications such as breast prosthesis, corneal grafts, dental implants, heart valves, hip and knee implants, intraocular lens, vascular grafts etc. The development of biomaterials used in medical devices has occurred in response to the growing number of patients affected with traumatic and non-traumatic conditions.

Bone is a dynamic organ that serves numerous functions within the body. The skeletal system serves as a means of anchoring muscles, tendons, and ligaments, thereby allowing locomotion. Bones such as the skull and ribs form protective barriers for the internal organs. Additionally, bones serve as a calcium reservoir, maintaining
homeostasis. They are also the source of hematopoiesis, thus giving rise to new blood and blood cells.

A number of materials have been examined for their ability to regenerate a new bone. Currently, antilogous bone remains the preferred material in bone graft and regenerative procedures. This bone, taken from a secondary site within the body is often excised and reimplanted. It contains both the inorganic mineral hydroxyapatite as well as the cell characteristics of bone. It is therefore a living substitute and can be remodeled into new and functional bone. Autografts may be combined with supplementary agents such as growth factors or synthetic bone replacement materials. The disadvantage of autologous bone usage is the creation of a secondary trauma sight that must be healed. Therefore, its usage is limited by availability. The materials taken from cadavers (allograft) and are not constrained by supply. This leads to voids cellular materials when it is implanted. The above materials are often demineralized, leaving behind a collagenous scaffold for the growth of a new bone. Further, it fails to function as a proactive material. These materials always carry the risk of disease transmission with them.

The optimisation of the composition in each bioactive glass and glass ceramics systems employing the in vitro experimental studies by soaking the glass and glass ceramics for different time periods, in a Simulated Body Fluid (SBF) whose ion concentration is similar to the human blood. The biocompatibility will be tested by studying the formation of Ca, P rich layer by soaking in different SBF solutions. The determination of mechanical properties and their relation with the change in microstructure, stability and strength in comparison with natural bones is essentially required to understand the mechanical performance along with the biocompatibility
which provides a complete solution for the optimisation of glass and glass ceramics for different biomedical applications.

Even though, several techniques are available, the ultrasonic velocities and attenuation measurement is suitable for the complete characterisation of materials both from scientific and technological point of view. The application of a shearing force to solid is met with considerable resistance. Since the glass products critically depend upon the solid like behaviour of glass, the elastic properties of solids are very important for the complete characterisation of solid material. There are three categories for determining the elastic moduli of solids namely, stress-strain curve, based upon the propagation of ultrasonic waves and the estimation of natural frequencies.

This proposed work is to synthesis the bioactive glass by normal melting quench method and to study the structural properties of the prepared sample through ultrasonic pulse echo technique. Further, we proposed to optimise the prepared glass samples for implant application using ultrasonic velocity measurements, pH value, SEM micrograph and FTIR spectroscopy.

**Experimental**

In the present work, the bioactive glasses of different series with different additives have been prepared with a constant phosphate and calcium ratio (P/C=1.5). The additives (Y) such as transition metal oxides, alkaline earth metals etc. have been varied from 0 to 10 mol% by replacing Na$_2$O content in all the serious of glasses. The different series of glasses 45P$_2$O$_5$-30CaO-(25-x) Na$_2$O-xY (x varies from 0 to 10 mol%) have been prepared from commercially available raw materials (Aldrich) using the normal melt quench method. 20g of each sample has been prepared for various studies and the weight ratio.
### Table 1: Experimental studies on bioglass system

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The components of analytical grade have been used without any further purification. The required chemicals have been weighed using a digital balance (Sartorius, Model: BP221S, USA.) having an accuracy of ± 0.1 mg. The weighted chemicals were put into the agate mortar and ground for about 2 h. The homogeneity of the mixture of chemicals was achieved by repeated grinding. Then, the mixture was preheated for 3 h in air at a temperature well below the melting temperature of the individual chemical in order to remove the contents such as H₂O, CO₂ etc. The preheated mixture was again ground for 3 h to reduce so as to get a common melting temperature of the mixture.

From the prepared glasses, six pieces (rectangle) have been cut using a diamond saw for ultrasonic velocities and attenuation measurements. Plane parallelism between the opposite faces of the glasses has been ensured before the actual measurements and checked employing a surface plate and dial gauge. The percentage of error in the measurement of glass thickness is ± 0.01 %. In the present investigation, glasses were shaped in the form of disc of 10 mm diameter and 6 to 7 mm thickness. The opposite faces of the disc shaped glasses were highly polished using lapping papers. The foreign particle residues on the surface of glass sample were removed by rinsing with acetone, followed by rinsing with ethanol.

**Density measurements**

Archimedes principle was employed to measure the density of all bioactive glass using CCl₄ as buoyant. The density of glass was obtained using the relation, The experiment was repeated for five times to get the accurate value of density. The overall accuracy in the density measurement is ± 0.5 kg m⁻³. The percentage error in the measurement of density is ± 0.05 %. 
Ultrasonic velocity and attenuation measurements & Elastic constants

The longitudinal and shear ultrasonic velocity measurements have been carried out in all glasses using the cross correlation technique employing the pulse echo method. Ultrasonic process control system with a 100 MHz digital storage oscilloscope and a computer were employed to record the ultrasonic (rf) signals. X and Y-cut transducers operated at a fundamental frequency of 5 MHz were used both for the generation and detection of the longitudinal and shear waves respectively. The ultrasonic velocity \( U \) in glass was obtained using the relation

\[
U = \frac{2d}{t} \text{ ms}^{-1}
\]  

(2)

where \( d \) is the thickness of the glass and \( t \) the precise transit time. The percentage of error in the measurement of velocity is \( \pm 0.1 \% \).

From the measured values of density \( (\rho) \), longitudinal \( (U_L) \) and shear \( (U_S) \) velocity in all the glass samples, the longitudinal (L), shear (G), Young’s (Y) and bulk (K) modulus, and Poisson’s ratio \( (\sigma) \) have been determined employing the standard relations.

In vitro studies

The in vitro studies were made to explore the bioactivity of all the prepared glasses. The SBF has been prepared in the lab whose pH value is equivalent to the pH value of the human blood plasma. The analytical grade chemicals (Aldrich, purity > 99.95%) have been added suitably with continuous stirring in a polyethylene container to prepare the SBF solution. Both the biocompatibility and the structural changes on the surface of the glass samples before and after soaking in SBF have been characterised by SEM and FTIR studies.
pH measurements

The variation in pH values of SBF were measured in all the 21 days employing a pH meter in all glasses under identical conditions. The pH electrode has been calibrated using the standard pH of 4.01, 7.01 and 10.1 before doing pH measurements. The percentage of error in the measurement of pH is ±0.005%.

Scanning Electron Microscopy

The scanning electron microscope (Hitachi, Model-514A, Japan) has been used to obtain surface image of all the glass samples to explore the glassy nature and the surface morphology. However, in case of bioactive glasses, the apatite layer formation has been found by SEM. Thus, from the micrographs obtained using SEM microscope, the silica-rich layer and Ca, P layers formed on the bioactive glasses have been identified.

Fourier Transform Infra Red analysis

Infrared absorption of the powdered glass samples have been analysed from the FTIR patterns. FTIR absorption spectra have been recorded at the room temperature from 4000 to 400 cm\(^{-1}\) using FTIR (Shimatzu, Model-8700, Japan) spectrometer. A sample each of 4.0 mg has been mixed with 200 mg of KBr in agate mortar and then, pressed into pellet of 13 mm diameter. For each sample, the FTIR spectrum has been normalised with the blank KBr pellet. The above studies have been made in all glass compositions before and after completing \textit{in vitro} studies.

\textit{In vitro} bioactivity of zirconium doped phosphate glass system

The 45P\(_2\)O\(_5\)-30CaO-(25-\(x\))Na\(_2\)O-\(x\)ZrO\(_2\) glass for different compositions (\(x = 0, 0.25, 0.5, 0.75\) and 1.0 mol\%) have been prepared using commercially available chemicals employing the normal melting quench method. The glasses with
ZrO₂ content x = 0, 0.25, 0.5, 0.75 & 1.0 mol% (here after termed as PCNZ0, PCNZ0.25, PCNZ0.5, PCNZ0.75 & PCNZ1.0 respectively) have been prepared. The P₂O₅-Na₂O-CaO-ZrO₂ glass system with different ZrO₂ contents from 0 to 1.0 mol% in place of Na₂O have been prepared with a fixed content of P₂O₅ (45 mol%) and CaO (30 mol%) by keeping the ratio of P/Ca as 1.5. The observed minima in density, velocities, modulus and a maxima in attenuation with change in ZrO₂ content confirms the softening of glass network up to 0.75 mol% of ZrO₂ content beyond which an increase in the compactness of glass network with further addition of ZrO₂ content has been noticed. The observed results confirm the breaking of P-O-P network leads to the formation of NBO network. The results beyond 0.5 mol% of ZrO₂ confirms the reinforce of the glass structure due to ionic cross linking between NBOs. The pH value is increased for the first three days because of the instantaneous release of sodium ions. After the third day, the phosphate ion starts to release and dominate the acidity due to phosphate molecules. Therefore, a random change from 3rd day onwards has been noticed. All the glasses have similar trend of non uniform pH variations while PCNT0.75 glass shows higher pH value which proves the existence of higher bioactivity. The observed absorption bands in all the in vitro glass at 3430 and 1630 cm⁻¹ band confirms respectively the presence of OH groups and the calcium apatite crystal. Further, SEM studies also confirm the existence of hydroxyapatite layer in all the glass samples. It is inferred from the above studies that all the prepared glasses are bioactive in nature. However, the higher bioactivity has been recorded in 45P₂O₅-30CaO-24.25Na₂O-0.75ZrO₂ glass than the other compositions.
Effect of TiO$_2$ on the bioactivity of phosphate based glass system through *in vitro* and ultrasonic studies

The 45P$_2$O$_5$-30CaO-(25-x)Na$_2$O-xTiO$_2$ glass for different compositions ($x = 0$, 0.25, 0.5, 0.75 and 1.0 mol%) have been prepared using commercially available chemicals employing the normal melting quench method. The phosphate based glasses with different TiO$_2$ contents $x = 0$, 0.25, 0.5, 0.75 & 1.0 (hereafter termed as PCNT0, PCNT0.25, PCNT0.5, PCNT0.75 & PCNT1.0 respectively) have been prepared. TiO$_2$ doped phosphate glass systems at a fixed composition of P/Ca for different TiO$_2$ contents (0.25, 0.5, 0.75, 1.0 mol% by replacing by Na$_2$O) have been prepared for optimisation of their bioactivity. It is evident from the present observation that the TiO$_2$ is used to obtain the glasses with increasing packing density, controlled solubility and increased bioactivity. The ultrasonic velocities and attenuation measurements showed that the structural changes performed during addition of TiO$_2$ content. The initial addition of TiO$_2$ in the well packed glass network helps to modify the structure leading to a loose packing as decrease in evidenced by the elastic moduli. The observed sudden modification in the structure leads to increases in the solubility during *in vitro* studies. Thus, a PCNT0.25 exhibits a poor bioactive nature. Glass with a high TiO$_2$ content has owned a controlled soluble nature. An increase in the glasses stability, controlled solubility and good bioactive has been evidenced with increase in TiO$_2$ content from 0.5 to 1 mol%. FTIR studies showed that the glass sample PCNT1 has a strong absorption band for hydroxyapatite layer. The SEM micrograph also conforms the formation of rich Ca-P layer on the surface of the glass sample PCNT1. The above studies explores that the glass with 1.0 mol% of TiO$_2$ (PCNT1) show better stability with controlled solubility and good bioactive nature among the other prepared glasses.
Physicochemical properties of MgO added glasses for biomedical applications

The 45P₂O₅-30CaO-(25-ₓ)Na₂O-ₓMgO glass for different compositions (ₓ = 0, 1, 2.5, 5 and 10 mol%) have been prepared using commercially available chemicals employing the normal melting quench method. The different MgO contents (x = 0, 1, 2.5, 5 and 10 mol% (here after termed as PCNM0, PCNM1.0, PCNM2.5, PCNM5 & PCNM10 respectively) of the glasses have been prepared. In the present investigations, P₂O₅-CaO-Na₂O glass samples with different MgO (replacing Na₂O) content by keeping C/P ratio as 1.5 has been prepared and characterised employing the studies such as ultrasonics, FTIR, SEM, pH studies etc. The observed minimum in density, velocities, and modulus and a maximum in attenuation with change in MgO content indicate the softening of glass network up to 1 mol% of MgO content. The addition of MgO content up to 2.5 mol% increase the structural compactness of glass network. Further, the addition of MgO beyond 2.5 mol% results a loose packing of atoms leading to the structural softening have been noticed. The ultrasonic velocities and attenuation measurements reveals the same trend as that of density. After the third day of in vitro, the phosphate ion starts to release and dominate the acidity due to phosphate molecules. Therefore, a random change from 3rd day onwards has been noticed. All the glasses have similar trend of non-uniform pH variations, while the PCNM2.5 glass shows a higher pH value which proves the existence of higher bioactivity. The in vitro studies reveal that the controlled solubility took place for the sample with 2.5 mol% of MgO content. The observed absorption bands in all the in vitro glass at 3430 and 1630 cm⁻¹ band confirms respectively the presence of OH groups and the calcium apatite crystal. The above studies confirm the existence of the OH vibrations in the glass samples with the addition of low MgO content. i.e., below 5 mol%, beyond which the OH vibrations are not presented. The FTIR studies proved
that the presence of hydroxyapatite layer in all the prepared samples. However, the SEM studies reveal a strong and porous hydroxyapatite layer in the sample PCNM2.5. It is inferred that PCNM2.5 containing glass sample showed the higher bioactivity than other samples.

**Formation of hydroxyapatite layer in Ag₂O added phosphate based glasses**

The 45P₂O₅-30CaO-(25-x)Na₂O-x Ag₂O glass for different compositions (x = 0, 0.25, 0.5, 0.75 and 1mol%) have been prepared using commercially available chemicals employing the normal melting quench method. The different Ag₂O contents x = 0, 0.25, 0.5, 0.75, 1mol% (hereafter termed as PCNA0, PCNA0.25, PCNA0.5, PCNA0.75 & PCNA1.0 respectively) of the glasses have been prepared. The P₂O₅-Na₂O-CaO-Ag₂O glass system with different Ag₂O contents from 0 to 1.0 mol% in place of Na₂O have been prepared with a fixed content of P₂O₅ (45 mol%) and CaO (30 mol%) by keeping the ratio of P/Ca as 1.5. The initial addition of Ag₂O content up to 0.5 mol% decreases the density of the glass leads to break the networks and the formation of NBOs. The further addition of Ag₂O may be act as the intermediate in the network results increase the packing density, controlled solubility and increased bioactivity. The ultrasonic velocities and attenuation measurements showed that the structural changes performed during addition of Ag₂O content. The initial addition of Ag₂O up to 0.5 mol% in the well packed glass network helps to modify the structure leading to a loose packing as decrease in evidenced by the elastic moduli. The observed sudden modification in the structure leads to increases in the solubility during *in vitro*. The pH value is increased for the first three days because of the instantaneous release of sodium ions. After the third day, the phosphate ion starts to release and dominate the acidity due to phosphate molecules. All the glasses have similar trend of non uniform pH variations during *in vitro*. The PCNA1 glass shows a
higher pH value at the end of *in vitro*. This proves the existence of higher bioactivity of the sample PCNA1. The observed absorption bands in all the glasses at 3430 and 1630 cm\(^{-1}\) band confirm respectively the presence of OH groups and the calcium apatite crystal. Further, SEM studies also confirm the existence of hydroxyapatite layer in all the glass samples and PCNA1 glass sample shows better Ca-P rich layer than the other samples. The studies support well for the growth of better Ca-P rich layer over PCNA1 glass sample. It is inferred from the above studies that all the prepared glasses are bioactive in nature. However, the higher bioactivity has been recorded in glass sample PCNA1.

The following are the scope of the present thesis

- In all the prepared glass samples with different transition metal oxides, a particular composition namely PCNT1 has been identified with greater bioactivity from all the glass systems. Thus it confirms the requirement of optimisation procedure to explore a suitable bioactive glass for implant applications.

- It facilities to explore the information such as structural changes, stability etc., which are required for the optimisation of the bioactive glass for different biomedical applications.

- Proposed techniques can also be used for characterization of bioactive glasses.

- Suitable composition of these bioactive glasses allows the synthesis of the materials with a controlled solubility, their superficial degradation mechanism allows them to maintain the mechanical properties during the degradation period.

- The analysis of the *in vivo* biological response of silver doped bioactive glasses are the future focus of the research.

- This technique can also be used nano phase materials through an approximate sample preparation. This may improve the bioactivity of the glass samples.
LIST OF PUBLICATIONS

- **G. Rajkumar, S. Aravindan and V. Rajendran**
  
  *In vitro* bioactivity of zirconium doped phosphate glass system.

  *Journal of American Ceramic Society, 2008 (Communicated).*

- **G. Rajkumar, S. Aravindan and V. Rajendran**
  
  Effect of TiO$_2$ on the bioactivity of phosphate based glass system through *in vitro* and ultrasonic studies.

  *Journal of Material Science: Materials in Medicine, 2008 (Communicated).*

- **G. Rajkumar, S. Aravindan and V. Rajendran**
  
  Development of MgO doped phosphate glasses for biomedical applications.

  *Journal of Non-Crystalline Solids, 2008 (Communicated).*

- **G. Rajkumar, B.Sraravanakumar S. Aravindan, and V. Rajendran**
  
  Formation of Hydroxyapatite layer in Ag$_2$O added phosphate based glasses.

  *Philosophical Magazine B, 2008 (Communicated).*

- **V. Rajendran and G. RajKumar**
  
  Structural role of tellurium atoms in TeO$_2$-B$_2$O$_3$ glassy system through ultrasonic studies.

  *Proceeding of National Symposium on Acoustics, October 22-24, 2002.*
• G. RajKumar and V. Rajendran

Influence of zirconium on the properties of phosphate based bioactive glasses.


• G. RajKumar, S. Aravindan and V. Rajendran

The Role of Ultrasonic velocity and Attenuation Measurements in the Structural Property on the Phosphate Based Glass Sample


• G. Rajkumar, S. Aravindan and V. Rajendran

Effect of TiO₂ on the bioactivity of phosphate based glass system through in vitro and ultrasonic studies.