


Chapter 4

New Generation of Glass Materials for Biomedical Applications: Properties, Structure, Bioactivity, and Viability

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ABSTRACT

The limited strength of bioglasses has confined their application to non-load-bearing contexts, thus necessitating enhancements in their mechanical properties. A viable approach to surmount this hurdle involves integrating nitrogen into the silicate network of the glass. This outlines the effect of nitrogen addition in bioglasses of the system $\text{SiO}_2\text{-Na}_2\text{O-CaO}$. The purpose is to determine the effects of nitrogen addition on the physical and mechanical properties and the structure of oxynitride bioglasses based on the system $\text{Na}_2\text{O-CaO-SiO}_2\text{-Si}_3\text{N}_4$. Properties were all observed to increase linearly with nitrogen content. These increases are consistent with N in the glass structure in 3-fold coordination with silicon and extra cross-linking of the glass network. These increases are consistent with the incorporation of

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N into the glass structure in three-fold coordination with silicon with result in extra cross-linking of the glass network.

1. INTRODUCTION

Understanding the physico-chemical properties of biomaterials is crucial in the design of bone implants. The biomaterials used can include metals, alloys (such as 316L), polymers (e.g., silicones), natural materials (such as corals), and ceramics (e.g., hydroxyapatite, calcium phosphates, and glasses). The most well known glass in this context is Hench's Bioglass®, which has a mass chemical composition of 45SiO₂-24.5CaO-24.5Na₂O-6P₂O₅. These glasses are notable for being reactive biomaterials, also known as bioactive materials. This means that these materials can establish an intimate and stable chemical bond with living tissues. Currently, bioactive glasses are primarily applied in the field of auditory implants. However, their use as bone substitutes is pending due to their lower mechanical properties compared to bioceramics, leading to the innovative idea of enhancing bioactive glasses by introducing nitrogen. Oxy-nitride glasses were discovered in the 1980s as an intergranular phase in silicon nitride-based compounds densified in the presence of sintering additives. The liquid phase, formed with silica and the necessary sintering additives, facilitates the dissolution-diffusion-precipitation of beta-silicon nitride and appears at grain boundaries in the form of glass. Analysis of this glass revealed the presence of nitrogen substituting oxygen in the network, with a valence of three instead of two, which induces network densification. Numerous studies on these oxy-nitride glasses have shown that small additions of nitrogen lead to increases in the glass transition temperature, thermal expansion coefficient, density, viscosity, elastic modulus, hardness, and toughness of the glass. More recent research has also demonstrated a significant increase in flexural strength. There is an increasing focus on developing bioactive glasses for applications in repairing or replacing bone (Hench., 1991). These materials are designed to foster a positive tissue response, stimulate new tissue growth, and interact with cells effectively (Kokubo et al., 2003; Fujibayashi et al., 2003; Liang et al., 2006). The clinical success of Bioglass® (Hench et al., 1971) and dense hydroxyapatite ceramics (Badr et al., 2024) has spurred efforts to find new bioactive glasses and glass-ceramics with improved properties. Bioactive materials (Kokubo, 1991; Bachar et al., 2013) are known to bond with living bone by forming an apatite layer on their surface (Neo et al., 1992; Hill, 2004). Specifically, in vivo studies on phosphate-containing Bioglass® particles (100–300 µm) used to fill bone defects have demonstrated more significant new bone growth in the initial weeks post-surgery compared to hydroxyapatite particles (Kozo et al., 2000). Comparable bone in-growth has been reported for phosphate-free glass particles of the same size in the SiO₂-CaO-Na₂O system (Fujibayashi et al., 2003). Nevertheless, the limited mechanical strength and inherent brittleness of these bioactive glasses have constrained their use to non-load-bearing applications, such as ossicles in the middle ear (Mabrouk et al., 2018). One approach to addressing the low strength of these glasses is to incorporate nitrogen into the silicate network (Mabrouk et al., 2018; Hampshire, 2008). Research has indicated that substituting oxygen with nitrogen in alumino-silicate glasses leads to a linear increase in glass transition temperature, elastic modulus, and hardness with higher nitrogen content (Bachar et al., 2016; Hampshire and Pomeroy, 2008). Further studies have confirmed that nitrogen enhances the mechanical properties of potentially bioactive glasses (Bachar et al., 2016). It has been concluded that nitrogen acts as a network-forming anion, with its effects on glass properties being independent of other modifiers (Mabrouk et al., 2018). The addition of fluorine, such as in the form of CaF₂, to bioglass coatings lowers

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