Journal of the Korean Ceramic Society
Vol 26, No.6, PP.850~854, 1989

실험보고

Elastic Moduli and Dissolution Rates of Resorbable Na_2O-MgO-P_2O_5 Bioglasses

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(Received August 31, 1989)

Na_2O-MgO-P_2O_5 생체 유리의 탄성계수와 용해도

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(1989년 8월 31일 접수)

ABSTRACT

The elastic moduli and dissolution rates of 15 glasses with different mole ratios of sodium-magnasium -phosphate as potential non-toxic biomaterials were investigated. In this study, a 3-point bending test, sonic resonance technique, and theoretical calculation were used to evaluate the modulus of elasticity. The dissolution rates at 37℃ (human body temperature) were determined by the measurement of mass changes in each sample for 24 weeks.

요 약

인체에 무해한 생체 재료에 대한 연구로 Na_2O-MgO-P_2O_5 유리의 탄성계수와 용해도를 15가지 성분에 따라 조사하였다. 이 연구에서 탄성계수는 3-point flexural test, sonic resonance technique, 그리고 이론적 계산으로 구했다. 용해도는 37℃ 용액속에서 24주 기간 동안 시편의 질량 변화로 알아 보았다.

INTRODUCTION

The recent emphasis on the development of new materials for the application in human internal prostheses has brought a noticeable attention to glass as a candidate material. The need for research concerning implantable materials was initiated when physicians attempted to leave nonbiological materials embedded in the body following surgery. The reaction of tissue with man-made materials as well as any degradation of this material in such a hostile condition becomes very important to the appropriate material selection. Soluble glasses have been given much attention as a candidate for implant materials to achieve further improvements in biomaterials and device applications. Glass-ceramics based on phosphate glasses might be more suitable than those derived from the silicate systems and the possibility also exists of using microporous materials[1,2].

The potential of ceramics as biomaterial systems is due to their mechanical properties and resistance to chemical attack. At the present time, orthopedic fixation implants are made of stainless steel, other metals or plastic composites. These materials can lead to a loss in bone mass due to stress shielding. A disadvantage of ceramic material is that they can be broken before bone healing due body motion. The other problem is that ions dissolved from the implant cause local irritation and are believed to interfere with human body's immune system. In addition, some devices must be removed as soon as the need for surgical implant is finished[3,4].

None of these techniqes are entirely satisfactory and eventual loosening and separation of prothesis from tissue usually results. It is therefore desirable to develop stiff, resorbable and compatible materials which will dissolve at a rate proportional to bone healing. In addition, the dissolution should not release products which would promote a toxic response. The purpose of this preliminary study was to determine the elastic moduli and dissolution rates of sodium -magnesium-phosphate glasses, which are very strong candidates for the criteria decribed above.

EXPERIMENTAL PROCEDURE

Starting Materials

The composition of each glass chosen for this study is given in Table 1. The starting materials were Na_2CO_3*, $MgCO_3$*, and phosphoric acid*. Glass batches were preheated at 500℃ for 1 hour to allow volatilization of CO_2 and H_2O gases. The temperature was then increased to 1000-1200℃, depending on the compositions. MgO addition caused the glass to become more viscous. The glass melts were poured into a steel mold which was preheated to 300℃ in order to inhibit breakage due to thermal shock. A mold release chemical spray agent** was also used to prevent glass from adhering to the mold.

Table 1 Chemical Compositions of 15 Glasses

SERIES I	Glass #1	$Na_2O \cdot 3P_2O_5$
	Glass #2	$0.75Na_2O \cdot 0.25MgO \cdot 3P_2O_5$
	Glass #3	$0.50Na_2O \cdot 0.50MgO \cdot 3P_2O_5$
	Glass #4	$0.25Na_2O \cdot 0.75MgO \cdot 3P_2O_5$
	Glass #5	$MgO \cdot 3P_2O_5$
SERIES II	Glass #6	$Na_2O \cdot 2P_2O_5$
	Glass #7	$0.75Na_2O \cdot 0.25MgO \cdot 2P_2O_5$
	Glass #8	$0.50Na_2O \cdot 0.50MgO \cdot 2P_2O_5$
	Glass #9	$0.25Na_2O \cdot 0.75MgO \cdot 2P_2O_5$
	Glass #10	$MgO \cdot 2P_2O_5$
SERIES III	Glass #11	$5Na_2O \cdot 7P_2O_5$
	Glass #12	$3.75Na_2O \cdot 1.25MgO \cdot 7P_2O_5$
	Glass #13	$2.50Na_2O \cdot 2.50MgO \cdot 7P_2O_5$
	Glass #14	$1.75Na_2O \cdot 3.25MgO \cdot 7P_2O_5$
	Glass #15	$5MgO \cdot 7P_2O_5$

Property Measurements

The theoretical Young's modulus [E] was determined by Yamane and Sakaino[5] method. The 3-point bending test (Eq.1) and sonic moduli test (Eq.2) were conducted according to ASTM[6,7]. The 10 samples were formed in the range of 100 mm×5 mm×6 mm for the flexural test and 120 mm×6 mm×8 mm for the resonant frequency test.

$$E = PS^3/4\,WT^3dl \qquad (1)$$

$$E = 96.517[L^3/WT^3]MQF^2 \qquad (2)$$

where P : load coordinate of the selected point
S : length of span(8 mm)
W : width of specimen at the center
T : thickness of specimen at the center
dl : deformation coordinate of the selected point
L : length of specimen
M : weight of specimen
F : resonant frequency of specimen
Q : correction factor for fundamental flexural mode.

All dissolution samples were made into rectangular slabs(3 mm×10 mm×10 mm) and fibers (radius=0.5 mm, L=30 mm). The measurement of dissolution

Table 2 Chemical Compositions of Hank's Solution

Sodium Chloride	16.00 gram
Mangesium Sulphate	0.82 gram
Potassium Chloride	0.80 gram
Sodium Bicarbonate	2 54 gram
Sodium Azide	0.20 gram
Glucose	4.40 gram
Potassium Dihydrogen Phosphate	0.20 gram
Water	2.00 liter

rates was carried out using Hank's solution, whose chemical composition is shown Table 2. The solution volume was 14 ml and was replaced every 7 days. Prior to the measurement of mass change, samples were dried at 104℃ for 2 hours. The mass was recorded to the nearest 0.1 mg. All specimens were kept in covered glass tubes in a water bath at 37℃.

RESULTS AND DISCUSSION

The computed elastic modulus values for 15 glasses are summarized in Fig 1. The highest mean value was 75 GPa by 3-point bending and 76 GPa by sonic resonance for the $0.5 Na_2O \cdot 0.5 MgO \cdot 2 P_2O_5$ glass. The $5 Na_2O \cdot 7 P_2O_5$ glass had the lowest Young's modulus, which was 30 Gpa by the bending test and 31 Gpa by the sonic technique. Each series shows the same trend shown in Fig 1. Therefore, the elastic modulus increases until the mole ratio of Na_2O : MgO becomes 1, and then decreases as the amount of MgO increases. In the theoretical calculation (Fig.1-C), the elastic modulus of the glass decreases as the amount of Na_2O increases in each series. Considerable error may exist in the theoretical value of the elastic modulus because it is difficult to get true densities of three component glasses. Evidently, the theoretical estimation of elastic modulus cannot be used for the phosphate glass system even if it is applicable for silicate glasses.

As a result of measuring the dissolution rates (Fig.2-a to 2-f), each glass was classified as being either readily soluble, moderately soluble, or durable.

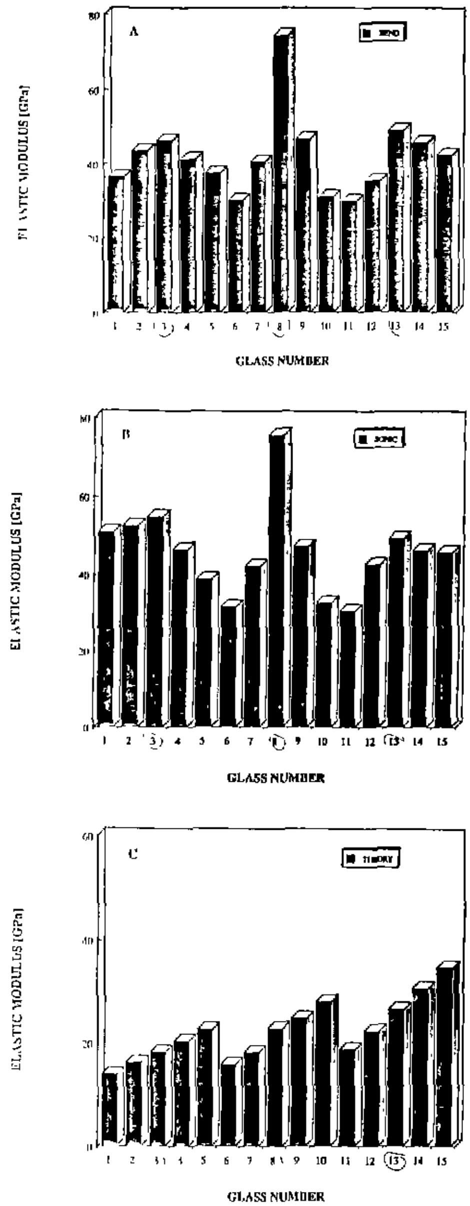

Fig. 1. Computed elastic moduli of 15 bioglasses by different techniques.

The readily soluble glasses are usually those having a high concentration of sodium oxide with no magnesium oxide. It was difficult to measure the dimensional changes of the specimens after the 6 th or 7 th week because of surface cracks and irregular thicknesses. The readily soluble glasses show over 50% weight loss

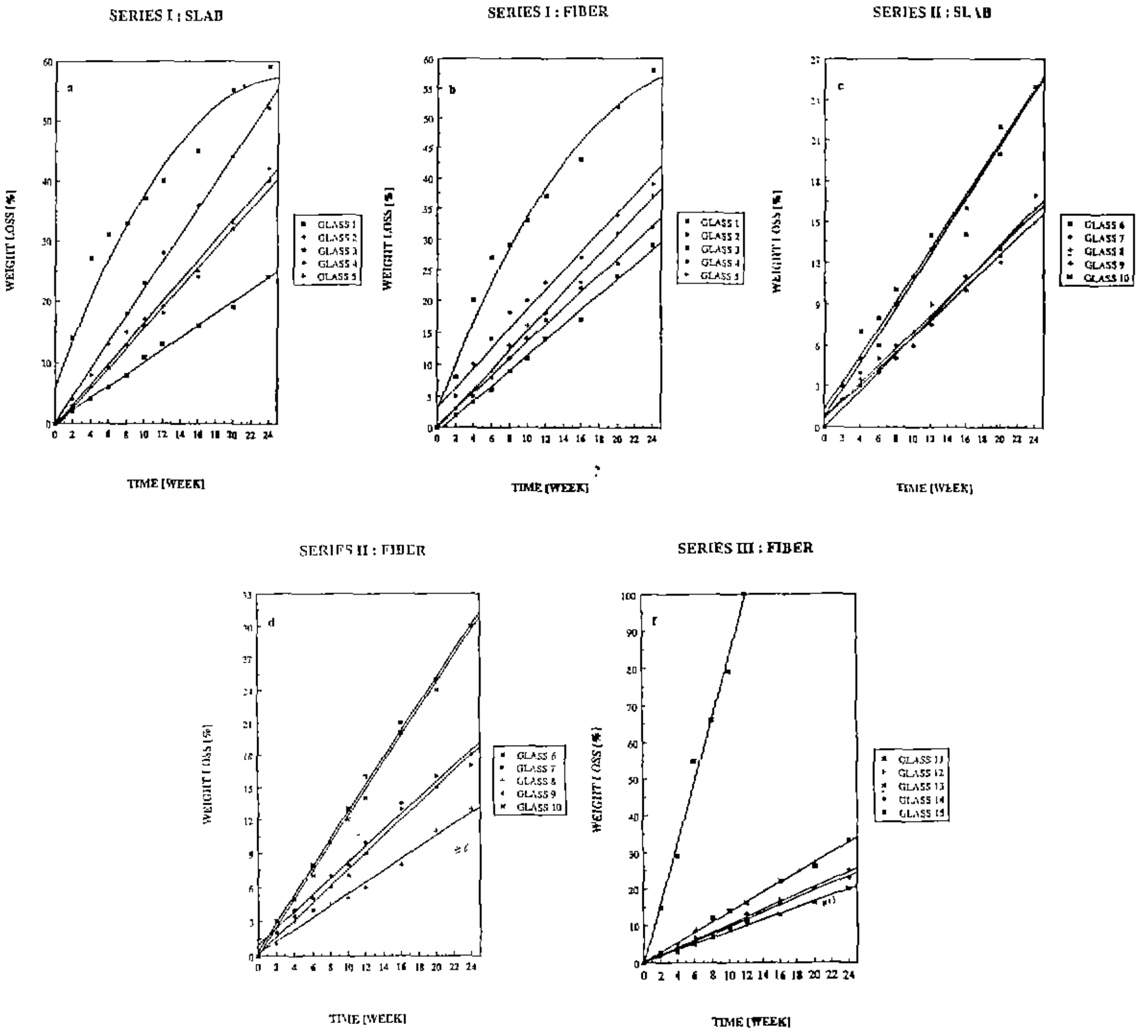

Fig. 2. Dissolution rates of slab and fiber glasses during 24 week period at 37℃.

after 24 weeks like glass #1, #2, and #11. The moderately soluble glasses exhibited weight losses of 30-40% during the same period. Finally, the durable glasses showed weight loss less than 20%.

The results can be explained by a combination of two factors ; 1) when the average chain length of the glass is incerased by decreasing the Na/P atomic ratio, the linear molecular ions forming the bulk of the glass become longer and more chain lengths are represented[8] ; 2) when more Na^+ ions are added, more non-bridging oxygens are created resulting in lower density and lower stiffness. In general, glasses with lower stiffness show a higher dissolution rate.

It is known that the elastic modulus of the compact cortical bone of the femur is 14 to 21 GPa[9,10]. Therefore, the stiffness of potential bioglass compared to bone should be above 20 GPa. The choice of bioglass is determined by the several factors such as bone healing time, position of application, and condition of fractured or cracked bone, etc. The Na_2O-MgO-P_2O_5 glass systems studied here can be used as resorbable implant materials which satisfy both functional and biocompatibility requirements.

SUMMARY

The elastic modulus of Na_2O-MgO-P_2O_5 glass incresed as the MgO content increased until the mole ratio of Na_2O : MgO reached unity. The $0.5\,Na_2O \cdot 0.5\,MgO \cdot 2\,P_2O_5$ glass showed the highest elastic modulus, but it had the lowest dissolution rate. Higher solubility was obtained when more sodium oxide was added. The $5\,Na_2O \cdot 7\,P_2O_5$ glass dissolved completely in 8 weeks after immersion in Hank's solution at 37℃.

It is difficult to say that dissolution rate depends on the elastic modulus of glass even though both properties are closely related with the structure and density of glass. It is not possible to neglect the apparent relationship between the modulus of elasticity and the dissolution rate(i.e.the higher elastic modulus, the lower the solubility).

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