

NATIONAL BUREAU OF STANDARDS REPORT

9916

Progress Report

on

X-RAY-OPAQUE REINFORCING FILLERS

FOR COMPOSITE MATERIALS



U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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X-ray-Opaque Reinforcing Fillers For Composite Materials

R. L. Bowen and G. W. Cleek

Clear, colorless glasses that absorb roentgen rays were prepared by melting together compounds yielding silica, boric oxide, alumina, barium oxide and barium fluoride. Barium made the glasses radiopaque, fluoride lowered the refractive indexes, and alumina tended to stabilize the glasses. These glasses are part of the reinforcing fillers for composite dental restorative materials.

Roentgenograms have been practically useless in the detection of the secondary caries or underlying decalcified dentin that might be a sequellae to the placement of unreinforced direct filling resins or the first composite materials to become available. This is due to the fact that these materials are relatively radiolucent; consequently, there has been a continued interest in means of making such restorative materials radiopaque.

The introduction of inorganic reinforcing fillers into resin restorative materials,¹ commonly called composite materials,² suggested the possibility of making such materials opaque to X-rays. This can be done by the incorporation of an element of relatively high atomic number or weight into the glass that constitutes part or all of the reinforcing filler. Many of such elements are not suitable because of the color they impart to the glass, or, in the case of lead, because of the possibility of discoloration through the formation of sulfides.

The purpose of this paper is to report investigations of various barium-containing glasses, especially formulated for use in dental composite materials.

Normally, the introduction of barium oxide into a glass formulation raises its refractive index. The commercially available glasses containing the required amount of barium have refractive indexes that are above optimum for the purposes of this application. Furthermore,

most commercial barium glasses contain alkali elements, such as sodium, potassium or lithium and these elements can catalyze the hydrolysis of silica.³ The presence of these monovalent alkali elements in a glass formulation, in the opinion of the authors, might be detrimental to the durability of the bond between the glass and the silane coupling agent. The quality of the bonding between the polymer and the filler particles determines whether or not the filler is a reinforcing filler, and is of utmost importance in determining the strength of the composite material.⁴

Since the introduction of the fluoride ion into glass formulations lowers the refractive index,^{5,6} it was important to determine if clear glasses having the proper value of refractive index could be formulated utilizing barium fluoride in the place of barium oxide. Other possible effects of the fluoride ion concentration³ remain to be determined.

MATERIALS AND METHODS

The formulations of the glasses that were prepared in this project are given in the Table. The glasses were melted in an electric furnace in a platinum crucible 6.35 cm in diameter by 7.62 cm deep. After the batch was melted, the melt was stirred with a motor-driven platinum 10%-rhodium double-bladed propeller-type stirrer to obtain homogeneity. The time of melting and fining depended on the characteristics of the melts as did the maximum temperature used. Usually, about 1.5 hours was required to fill the crucible and about the same length of time for stirring the melt. The maximum temperature used was about 1550°C but this was decreased to about 1150°C for the melts containing a relatively large amount of fluoride. A small amount of the molten glass was poured into a metal mold, and the rest was poured into clean water to quench the glass and break it up into small pieces so that it could be conveniently ground in a jar mill.

The refractive indexes were determined with a microscope by the oil-immersion method.

RESULTS

From the data given in the Table, it appears that clear glasses containing large proportions of barium fluoride can be prepared. Some of these compositions have refractive indexes close to those of the polymeric binders of current and experimental composite materials (n_D^{25} about 1.55; the refractive index of the polymeric binder varies somewhat depending on its chemical composition, extent of polymerization, water content and other factors).

Glasses containing 24 to 28 mole percent of barium fluoride or oxide, if used as the sole reinforcing filler for a dental composite material, yield materials that are more radiopaque than necessary. As a first estimate, about one part by weight of such a barium-containing glass (as a silane-treated powder) combined with two parts of silane-treated fused silica yields a composite restoration with a radiopacity intermediate between that of enamel and dentin.

The powder of one of these glasses (F1515) was passed through an oxygen-acetylene flame, converting the irregular-shaped particles into spheres. This was done because the use of rounded particle shapes and an intermittant size-distribution (gap grading) has been shown⁷ to give an increase in the powder-to-liquid ratio. However, as a result of this high temperature processing, the refractive index of the glass beads formed was higher than that of the starting material. Presumably, the molten glass particles had lost some of their fluoride, possible as volatile BF_3 or SiF_4 . Subsequently, a lower-temperature flame and a shorter residence time will be used to prepare spheres of the F1519-1 composition, which has been selected for further investigation.

DISCUSSION

An ideal glass for use as a reinforcing filler would have, among other desirable properties, a refractive index (to visible light) very close to that of the polymer matrix of the composite restoration. It should be colorless or have a color suitable for use in matching the color of the

composite material with that of the tooth. It should be transparent and have a low coefficient of thermal expansion. Since barium-containing glasses have higher thermal expansions than does fused silica, the total barium content of the composite should be no more than necessary to yield a composite with optimum radiopacity; one would expect this to fall in the range between that of enamel and dentin. Glass compositions that meet these particular requirements could not be found in the available literature.

A moderate alumina content has been shown to stabilize fluoride glasses against phase separation or devitrification that would be objectionable in this application.^{5,6} Formulations that yield two immiscible liquids in the molten stage must be avoided.⁸

It would be desirable to make use of the "boric oxide anomaly"⁹⁻¹⁴ and the less-well-known "alumina anomaly"^{10,12-14} to obtain a glass with the lowest possible

coefficient of thermal expansion. Whether or not a matching of the molar proportions of BaO and BaF₂ with the Al₂O₃ plus B₂O₃ in the glass^{13,14} gives a minimal thermal expansion has yet to be determined.

CONCLUSIONS

X-ray-opaque glasses can be prepared that are clear and colorless and that have refractive indexes suitable for use in composite restorative materials. The batch composition for one such glass, for example, is: SiO₂, 44; BaF₂, 28; B₂O₃, 16; and Al₂O₃, 12, in mole percent. The refractive index is influenced by the thermal history of the glass.

REFERENCES

1. Bowen, R. L.: Development of an Adhesive Restorative Material, in Adhesive Restorative Dental Materials II, University of Virginia Workshop, Public Health Service Publication No. 1494, 1966, pp 225-231.
2. Broutman, L. J., and Krock, R. H.: Modern Composite Materials, Reading, Mass: Addison-Wesley Pub. Co., 1967.
3. Alexander, G. B.: Polymerization of Monosilicic Acid, J Am Chem Soc 76:2094-6, 1954.
4. Bowen, R. L. Properties of a Silica-Reinforced Polymer for Dental Restorations, J Am Dent Assoc 66:57-64, 1963.
5. Cleek, G. W., and Scuderi, T. G.: Effect of Fluorides on Infrared Transmittance of Certain Silicate Glasses, J Am Ceramic Soc 42:599-603, 1959.
6. Tooley, F. V.: Handbook of Glass Manufacture. Vol. II, New York: Ogden Pub., 1960.

7. Bowen, R. L.: Effect of Particle Shape and Size Distribution in a Reinforced Polymer, J Am Dent Assoc 64:481, 1964
8. Charan, R.: Handbook of Glass Technology, 3rd Edition, Banaras (India): Banaras Hindu University Press, 1956.
9. Weyl, W. A., and Marboe, E. C.: The Constitution of Glasses, Vol. I, New York: Interscience Publishers, 1962.
10. Morey, G. W.: Properties of Glass, New York: Reinhold Publishing Corporation, 1954.
11. Hamilton, E. H.; Cleek, G. W.; and Grauer, O. H.: Some Properties of Glasses in the System Barium-Oxide Boric Oxide-Silica, J AM Ceramic Soc 41:209-215, 1958.
12. Galant, E. I.: Refractive Index and Coordination Transformation in Aluminoborosilicate Glasses, The Structure of Glass. Vol. 2, New York: Consultants Bureau, 1960, pp 451-453.

13. Appen, A. A., and Fu-si, Kan: Borate and Aluminoborate Anomalies of the Properties of Silicate Glasses, The Structure of Glass. Vol. 2, New York: Consultants Bureau, 1960, pp 445-450.
14. Demkina, L. I.: Additivity of the Properties of Silicate Glasses in Relation to Their Structure, The Structure of Glass. Vol. 2, New York: Consultants Bureau, 1960, pp 40-45, 472.
15. Levin, E. M., and Cleek, G. W.: Shape of Liquid Immiscibility Volume in the System Barium Oxide-Boric Oxide-Silica, J Am Ceramic Soc 41:175-179, 1958.

TABLE Compositions and Properties of Glasses Arranged

According to Decreasing Refractive Indexes

Glass No.	Composition of Batch (mole percent)					Refractive Index n_D	Appearance
	Al ₂ O ₃	BaF ₂	BaO	B ₂ O ₃	SiO ₂	Other	
EL722*			28	24	48		clear
F 700			28		66	6 ZnO	clear
Fl510		4	24	24	48		clear
Fl511		6	22	24	48		semi-opaline
Fl519		8	20	24	48		opaline
Fl512	3	8	20	24	45		clear
Fl252	10	2	25		63		clear
Fl513	4	12	16	24	44		clear
Fl149	10	4	20		66		clear
Fl150	10	6	18		66		clear
Fl515	12	20	8	16	44		clear
Fl523	4		7	17	56	{ 7 TiO ₂ 9 MgO	opaline and heterogeneous
Fl519†	12	28		16	44		clear
Fl511	10	8	16		66		clear
Fl514	3	8	12	24	53		opaline
Fl152	10	10	14		66		clear

Glass No.	Composition of Batch (mole percent)					Refractive Index n_D	Appearance
	Al_2O_3	BaF_2	BaO	B_2O_3	SiO_2	Other	
M3-4189†	12	28		16	44	1.554	clear
F1524	4		17	13	66	1.550	nearly clear‡
F1519-1†	12	28		16	44	1.548	clear
F1516	12	20		16	48	1.541	trace opalescence
F1522	12		15	16	57	1.540	nearly clear‡
M14-1441†	12	28		16	44	1.539 §	clear
						1.535	clear
F1527			17	17	58	1.536	opaline
F1526			17	13	62	1.528	opaline
F1520		28		8	43	1.518	opaline
F1521	8		7	12	73	1.500	nearly clear‡

* The data on Glass No. E1722 were taken from the literature⁸; the other data have not been published previously.

† Higher temperatures were used in the preparation of Glass No. F1519 relative to Glass No. F1519-1. Melt M14-1441 prepared in the Experimental Melting Department of Corning Glass Works was larger than their test melt M3-4189. Since these four glasses had the same batch composition, the differences in refractive index are presumably due to differences in retained fluorine with larger melts and lower temperature resulting in less volatilization of compounds such as BF_3 and SiF_4 .

‡ Contained small bubbles (seeds) and small crystalline contaminations of unmelted batch material (stones) due to high melt viscosity.

§ Annealed sample.

|| Quenched and jet pulverized.

