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Indentation testing of nuclear-waste glasses

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The fracture properties of several nuclear-waste glasses were determined by indentation techniques. The fracture toughness, K_{Ic}, was calculated from the measurement of radial cracks around Vickers diamond indentations as a function of applied load, and the results agree quite satisfactorily with values obtained by the Hertzian indentation technique. The fracture toughness of the waste glasses containing simulated fission products ranged from 0.9 to 1.1 MN $m^{-3/2}$ in air, with slightly higher values measured in dry nitrogen. The hardness was also obtained from the Vickers indentations and the ratio H/E was determined from the elastic recovery of Knoop diamond indentations. The values of E deduced from H and H/E were within 15% of values measured by ultrasonic tests. The results along with the limitations of the different techniques are discussed in detail.

1. Introduction

The fracture property of primary interest in nuclear-waste forms is the fracture toughness, K_{Ic}, since it is the most fundamental property characterizing the fracture behaviour. Although the fracture behaviour of nuclear-waste forms has received limited attention, it is recognized that premature failure or fracture, due to a decrease in K_{Ic}, could result in increased surface area available for leaching. Recent results have already shown that K_{Ic} of waste forms can be affected by radiation [1, 2] and localized composition changes [3]. Therefore, it is of interest not only to determine K_{Ic}, but also to measure the effects of radiation, temperature, and other processes or storage variables on K_{Ic}. This often necessitates the use of small specimens for which conventional techniques for measuring fracture toughness and other mechanical properties are impractical. In recent years, however, it has become apparent that indentation techniques offer the possibility of a relatively easy and rapid method for determinations of the fracture toughness of brittle materials. These techniques allow many measurements on a single specimen and also allow the localized evaluation of K_{Ic}, on the order of microstructural dimensions.

Although any sharp indenter will produce radial/median cracks in brittle materials, the Vickers diamond pyramid indenter has become the standard indenter because it consistently produces well-defined radial cracks emanating from the corners of the indentation [4, 5]. The deformation-fracture pattern for a Vickers indentation is depicted in Fig. 1. The load, P, produces a plastic impression with a characteristic diagonal of $2a_1$ and orthogonal radial cracks of characteristic length c. The technique of determining fracture toughness in brittle materials by direct measurement of radial cracks produced by Vickers indentations was first suggested on empirical grounds by Palmqvist [6, 7]. In 1976, Evans and Charles [4] derived a universal fracture-toughness curve based on extensive data that allowed the fracture toughness to be determined from the Vickers

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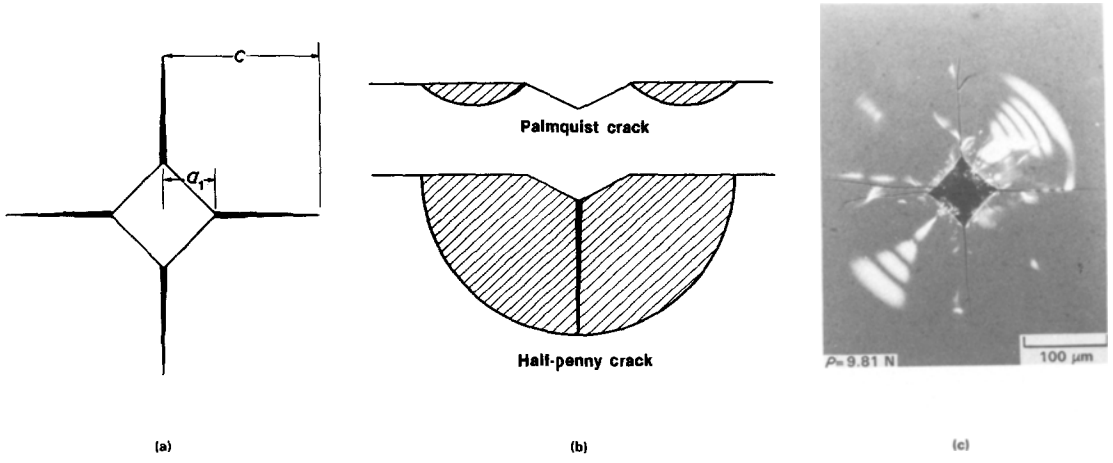


Figure 1 Vickers indentation geometry: (a) in-surface schematic showing indentation parameters, (b) cross-sectional schematic of both Palmqvist and half-penny cracks, and (c) micrograph of the Vickers-produced indentation-fracture system in MCC 76-68 waste glass at 9.81 N.

indentation parameters, providing the hardness, H, and Young's modulus, E, were known. In a later, more comprehensive analysis, Evans [5] showed that K_{Ic} can be expressed as

$$K_{Ic} = Ha_1^{1/2}(E/H)^{2/5}g(c/a_1) \quad (1)$$

where $g(c/a_1)$ is an empirical function obtained from a plot of the data compilation of Evans and Charles [4]. Based on comments of Marshall and Evans [8], $g(c/a_1)$ can be expressed as

$$g(c/a_1) = 0.057\,(c/a_1)^{-3/2} \quad (2)$$

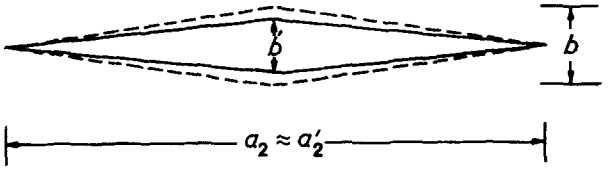
for large c/a_1. Others [9–12] have also derived similar expressions for K_{Ic}, differing primarily in the exponent of E/H or the proportionality constant. The $(c/a_1)^{-3/2}$ and E/H dependence of K_{Ic} have a theoretical basis in terms of the elastic/plastic indentation fracture mechanics of a half-penny crack [11, 12], and the particular form of $g(c/a_1)$ chosen for this study (Equation 2) is in closer agreement with existing glass data [9, 12] than other expressions [9, 10]. Although the theoretical basis for Equations 1 and 2 assumes well-developed half-penny cracks, Lankford [9] has recently suggested that Equation 1 and a slightly modified version of Equation 2 are valid over the entire range of indentation-crack morphologies, from Palmqvist crack formation to well-developed half-penny cracks. This contention is supported by the observations of Haranoh *et al.* [13] on soda–lime silica glass. Therefore, the correlation between K_{Ic} and indentation parameters can be made whether half-penny or Palmqvist cracks are produced.

The ratio E/H required in the determination of K_{Ic} can be determined from the calculated value of H ($H = 0.4636\,P/a_1^2$), if E is known. Alternatively, Marshall *et al.* [14] developed a simple indentation technique for measuring the hardness–elastic-modulus ratio, H/E, of elastic/plastic materials. The method is based on measurement of the elastic recovery of the in-surface dimensions of a Knoop diamond indentation, as shown in Fig. 2. Under a load P, the ratio of the diagonal dimensions, a_2 and b, at the contact surface is defined by the Knoop indenter geometry, where $a_2/b = 7.11$. Upon unloading, the elastic recovery reduces the length of the shorter dimension, b, to b', while the longer dimension, a_2, remains relatively unaffected. The recovery depends on the ratio H/E and is independent of load. Marshall *et al.* [14] have derived the following expression relating b'/a_2' to H/E:

$$b'/a_2' = b/a_2 - \alpha H/E \quad (3)$$

where $\alpha = 0.45$. The value of α was determined by fitting Equation 3 to data obtained for a wide range of materials with known H and E. We have also found Equation 3 with $\alpha = 0.45$ to be a good fit to our own data obtained on a range of materials with known H/E. The uncertainty in H/E determined by Equation 3 is estimated to be $\sim \pm 10\%$. Therefore, in principle, indentation testing alone can yield values of H, H/E and K_{Ic}.

The Hertzian indentation test has also been



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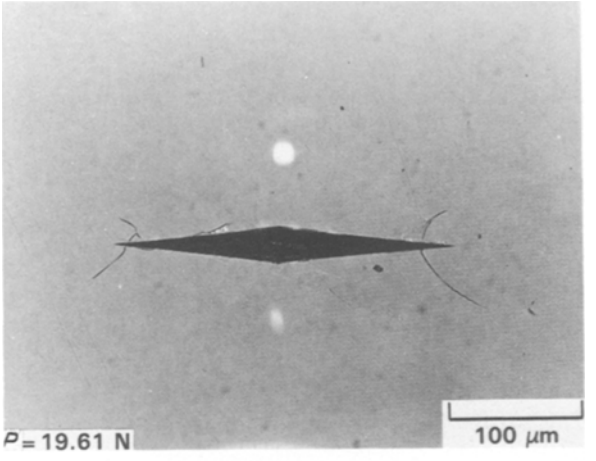
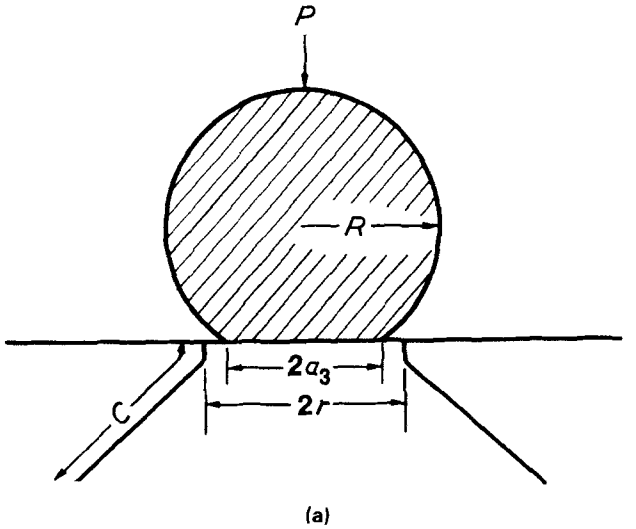


(b)

Figure 2 Knoop indentation geometry: (a) in-surface schematic illustration and (b) micrograph (MCC 76-68 waste glass) of a Knoop indentation.

used to determine the fracture toughness of brittle materials without any adjustable parameters [15]. In this technique, illustrated schematically in Fig. 3a, a spherical indenter of radius R under a load P produces a circular contact area of radius a_3 on the flat surface of a specimen. The contact radius, a_3, is given by

$$a_3 = (4\,kPR/3E)^{1/3} \tag{4}$$



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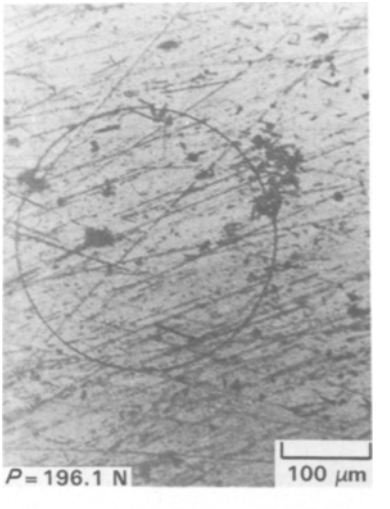

(b)

Figure 3 Hertzian indentation geometry: (a) cross-sectional schematic illustration and (b) micrograph of a Hertzian ring crack in GP 98/12 waste glass after etching with HF solution to reveal crack.

where k is given by the expression

$$k = (9/16)[(1-\nu^2) + (1-\nu'^2)E/E'] \quad (5)$$

where ν and ν' are the Poisson ratios of specimen and indenter, respectively, and E' is the Young's modulus of the indenter. Cone cracks of length c, which appear as rings of radius r on the surface (Fig. 3b), form whenever the load, P, approaches or surpasses the critical load, P_c. This critical load is defined as the load at which the probability for failure equals 50% and is determined from plots of fracture probability against load.

If the material contains an adequate flaw population, then Warren [15] has shown that the fracture-surface energy, γ_F, is related to P_c by the expression

$$P_c = \frac{\beta\gamma_F kR}{(1-\nu^2)} (a_3/c'')[\phi'']^{-2} \quad (6)$$

where β is a constant and $(a_3/c'')[\phi'']^{-2}$ is the crack-extension function which has been numerically evaluated for different values of r/a_3 and ν [15, 16]. The value of the constant β has been calculated to be $8\pi^3/27$, assuming that the cone crack has the same stress intensity factor as a plane internal crack [15]. This is an approximation which should be considered when comparing Hertzian data with results obtained by other techniques. The fracture toughness, K_{Ic}, is related to γ_F, assuming plane-strain crack extension, by the expression

$$K_{Ic}^2 = 2\gamma_F E/(1-\nu^2) \quad (7)$$

This technique has been used to measure K_{Ic} in several nuclear-waste materials [1–3]. In fact, good agreement between values of K_{Ic} determined by the Hertzian technique and the more conventional double-torsion technique has been achieved for nuclear-waste glasses [17], SiC [18] and a glass–ceramic [1].

The purposes of this paper are both technological and scientific. The technological objectives were to determine the fracture toughness of several nuclear-waste glass compositions by both Vickers and Hertzian indentation testing. Scientifically, the objective was to compare the results of the two techniques and to determine the applicability of the empirical relationship for determining K_{Ic} from Vickers indentations. Furthermore, independent measurements of H and E were made to determine if the estimate of the ratio H/E from Knoop indentation testing is valid. The correlations between fracture toughness and indentation testing have been established for only a few simple materials; therefore, the general utility of the formulation can be established only if a wide variety of materials, such as used in this study, are tested.

2. Experimental details

2.1. Materials and specimen preparation

The compositions of the glasses investigated are given in Table I. The MCC 76-68 material is from Bar No. 277 of the US Materials Characterization Center inventoried stock of this material. This glass was melted at 1250° C for 20 h, cast as a 25 × 25 × 300 mm bar, and stress-relieved at 550° C for several hours. Homogeneous specimens of SM 58 LW 11 and SM 513 LW 11 glasses were obtained from the Institut für Nukleare Entsorgung (INE), Kernforschungszentrum, Karlsruhe, as pieces from large-scale cast cylinders (300 mm diameter) which cooled by natural convection (~ 24 h). Strongly streaked specimens of SM 58 LW 11 (due to partial devitrification) which showed liquid–liquid segregation followed by crystallization of cristabolite (cooling time, 72 h) were also tested. The VG 98/12 and the GP 98/12 materials were also prepared at the INE [19], but were fabricated by melting well-mixed powders in crucibles at 1200° C for 2 h and casting into cylinders of about 25 mm diameter and 20–40 mm length. These glasses were cooled from 600 to 100° C over a period of 17 h.

The recrystallized GP 98/12 and GP 98/26 products were given a heat treatment at 750° C for 100 d which produced a fine dispersion of both needle-like crystals with an apatite-type structure (consisting mainly of CaO, CeO_2, Nd_2O_3, and P_2O_5) and flat crystallites of a calcium–titanium–silicate phase. (The GP 98/26 is identical with GP 98/12 except that it contains 3.7 wt % of Gd_2O_3 as a neutron poison.) The B1-3 glass ceramic is identical to that studied previously [1] and consists primarily of one or two crystalline modifications of celsian ($BaAl_2Si_2O_8$) and a rare-earth titanate ($RE_2Ti_2O_7$). Minor phases of scheelite (Ca, Ba, Sr) MoO_4 and a spinel (Ni, Fe, Cr)$_3O_4$ are also present.

The values of E and ν for these glasses were independently calculated from the longitudinal (20 MHz) and transverse (5 MHz) sound velocities measured using the echo-overlap technique. The moduli were isotropic. These values, along with the densities, ρ, and shear modulus, G, are given in Table II.

TABLE I Compositions of the nuclear-waste glasses (mol %)

	MCC 76-68*	VG 98/12	GP 98/12	SM 58 LW 11	SM 513 LW 11
SiO_2	52.64	58.5	54.9	57.14	52.45
B_2O_3	10.20	11.0	10.3	10.65	11.37
Al_2O_3	0.40	1.6	1.5	0.69	1.56
Li_2O	–	–	–	7.55	8.59
Na_2O	16.26	17.5	16.4	4.51	5.72
MgO	–	3.2	3.1	3.07	3.09
CaO	3.15	4.6	4.2	4.12	4.91
TiO_2	2.86	3.6	3.4	3.36	3.38
	85.51	100.0	93.8	91.09	91.07
Al_2O_3	–		–	0.54	0.54
BaO	0.26		0.30	0.04	0.04
CeO_2	0.42		0.44	0.06	0.06
Cr_2O_3	0.24		0.05	0.11	0.11
Cs_2O	0.34		0.23	0.03	0.03
Eu_2O_3	–		0.09	–	–
Fe_2O_3	4.39		0.10	0.63	0.63
Gd_2O_3	–		0.01	–	–
La_2O_3	0.93		0.11	0.02	0.02
Na_2O	–		–	3.20	3.21
Nd_2O_3	0.30		0.36	0.05	0.05
NiO	–		0.10	0.34	0.34
MnO_2 †	0.02		0.22	0.42	0.42
MoO_2	0.99		0.90	0.12	0.12
PdO	0.33		0.33	0.04	0.04
Pr_2O_3	–		0.10	0.01	0.01
Rb_2O	0.07		0.05	0.01	0.01
Rh_2O_3	0.04		0.04	–	–
RuO_2	–		0.53	0.07	0.07
Sm_2O_3	–		0.07	–	–
SrO	0.29		0.24	0.03	0.03
TeO_2	–		0.11	0.02	0.02
Y_2O_3	0.13		0.06	0.01	0.01
ZnO	4.31		–	0.01	0.01
ZrO_2	1.05		1.02	0.39	0.39
P_2O_5	0.33		0.44	< 0.01	< 0.01
SO_3	–		–	0.40	0.40
F	–		–	2.36	2.37
UO_2	–		0.28	–	–
CdO	0.03		–	–	–
PbO	0.02		–	–	–
	100.00		100.00	100.00	100.00

*Based on chemical analysis of the glass.
†For Tc.

Specimens of various geometries and thickness were cut with parallel surfaces in order to ensure that the indentations were perpendicular to the surface. The surfaces to be tested were polished to a 7-μm diamond paste finish (except as noted).

2.2. Technique

The Vickers indentations were made at loads of 0.98 N to 19.6 N with a microhardness testing machine in air and at 30 N with a Frank hardness machine within a glovebox containing a dry-nitrogen atmosphere. Three indentations were made at each load. The characteristic dimensions a_1 and c were measured immediately with an optical microscope. The Knoop indentations were made at a load of 30 N in the dry-nitrogen atmosphere with the same Frank hardness machine. Higher loads usually resulted in fracturing, which distorted the impressions. The Hertzian indentations were made with steel indentors ($E' = 210$ GPa and $\nu' = 0.29$) with the Frank hardness machine, as previously described [1–3, 16, 18],

TABLE II Measured values of ρ, ν, E, and G

Material	ρ (g cm^{-3})	ν	E (GPa)	G (GPa)
MCC 76-68 2.953	0.241	81.1	32.6	
VG 98/12 2.564	0.231	81.7	33.2	
VG 98/12 + Mo	2.577	0.230	80.6	32.8
GP 98/12 2.772	0.238	81.7	33.0	
GP 98/12 cryst.	2.813	0.239	81.8	33.0
GP 98/26 cryst.	2.799	0.239	81.4	32.6
SM 58 LW 11				
homogeneous	2.606	0.229	88.2	35.9
strongly streaked	2.609	0.226	88.3	36.0
SM 513 LW 11	–	–	89.1*	–
B 1-3 3.243	0.272	100.7	39.6	

*Value provided by L. Kahl, INE.

and the ring cracks were detected and measured by optical microscopy.

3. Experimental results

3.1. Vickers indentations

The hardness data as a function of load are shown in Fig. 4. Although there is some scatter in the data, the hardness is apparently independent of load. The average hardness (Table III), shown by the line through the data, is based only on the measurements in air with the microhardness machine in order to avoid any instrumental or environmental variations. From the data it is apparent that the hardness is not instrument- or environment- (air against dry nitrogen) dependent. Measurement of the cracks emanating from the corners of the hardness indentation showed that c increased as $P^{2/3}$ for all materials, as illustrated in Fig. 5 for several waste glasses that were tested over the widest range of loads. The calculated fracture toughness values based on Equations 1 and 2, with H/E determined from the average

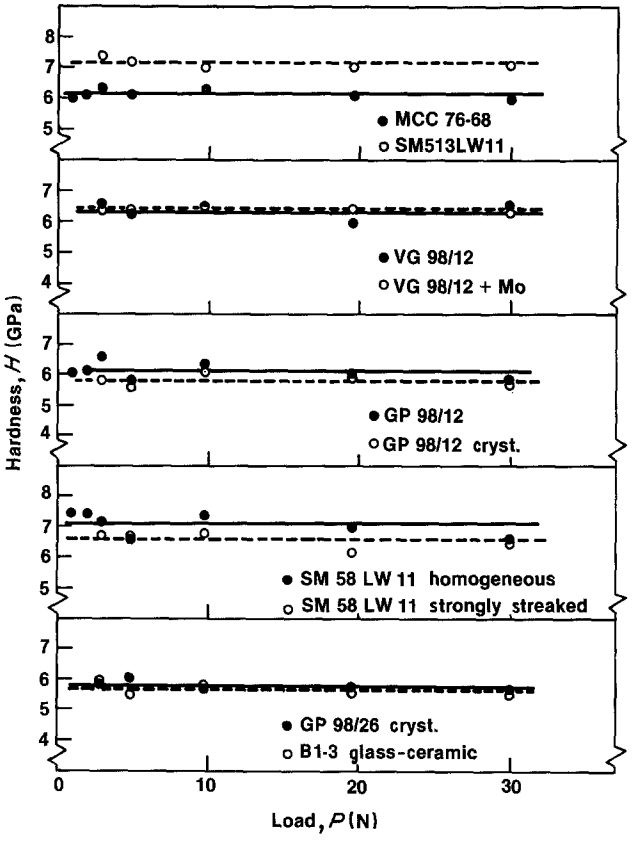

Figure 4 Vickers hardness, H, as a function of applied load, P, for different waste glasses.

TABLE III Summary of Vickers and Knoop indentation data

Material	H^* (GPa)	$H/E^\dagger$	$K_{Ic}{}^\ddagger$ (MN m$^{-3/2}$)	b'/a'_2	$H/E^\S$ (Knoop)	$E^\P$ (GPa)	$K_{Ic}{}^{**}$ (MN m$^{-3/2}$)
MCC 76-68 6.16	0.076	0.94	0.110	0.069	89.2	0.98	
VG 98/12 6.30	0.077	0.78	0.107	0.076	82.9	0.78	
VG 98/12 + Mo	6.39	0.079	0.78	0.107	0.076	84.0	0.81
GP 98/12 6.12	0.075	0.97	0.109	0.071	86.2	0.99	
GP 98/12 cryst.	5.83	0.071	0.93	0.104	0.081	71.5	0.88
GP 86/26 cryst.	5.81	0.071	0.99	0.105	0.080	72.7	0.94
SM 58 LW 11							
homogeneous	7.09	0.080	1.11	0.108	0.073	97.1	1.15
strongly streaked	6.57	0.074	0.93	0.105	0.079	82.9	0.91
SM 513 LW 11	7.17	0.081	1.02	0.105	0.080	89.7	1.02
B 1-3 glass–ceramic	5.70	0.057	1.41	0.117	0.053	107.5	1.45

*Average value determined from Vickers indentations.
†Determined using E from Table II.
‡Average value based on Equations 1 and 2, H, and H/E.
§Determined from b'/a'_2 using Equation 3.
¶E predicted from H/E (Knoop) and H.
**Determined using H/E (Knoop) instead of H/E.

value of H (Table III) and the measured value of E (Table II), are shown in Fig. 6. As with hardness, the average value of K_{Ic} (Table III) is shown by the line through the data and is based on the data obtained in air only. Some of the materials showed an apparent change in K_{Ic} when measured in dry nitrogen as opposed to the room (humid) air. In order to verify this effect, measurements were also made in dry N_2 after 21 and 30 days exposure to this atmosphere. The results of the air and nitrogen atmosphere measurements are summarized in Table IV. The results show a clear increase in K_{Ic} in the dry-nitrogen atmosphere. The time-dependence of the effect is the subject of another study to be reported later.

Although our analysis is assumed to be independent of crack morphology (Palmqvist against half-penny cracks), it is still of interest to define the crack morphology. Since all the waste glasses behave similarly, the MCC 76-68 glass was taken to be representative. Vickers indents at loads of 2.94, 4.90, 9.81 and 19.61 N were made and the crack patterns studied by serial polishing. At a depth beyond the indent impression, the cracks merged to form orthogonal cracks, as shown in Fig. 7. This pattern suggests that the cracks are half-penny shaped. One final point worth mentioning is that the radial cracks always appeared to precede any lateral cracking that occurred.

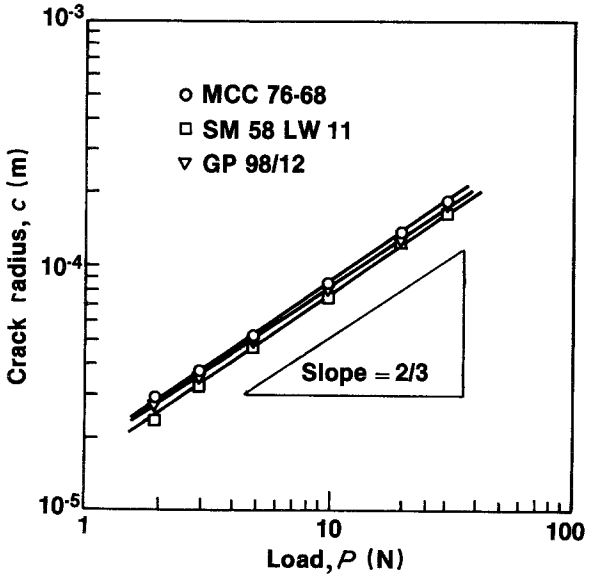

Figure 5 Crack length, c, as a function of applied load, P, for Vickers indentations.

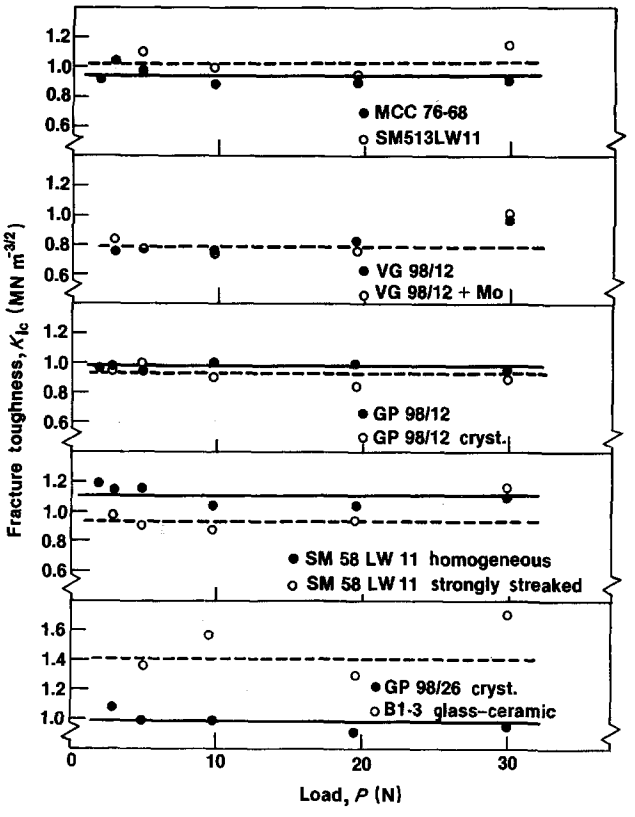

Figure 6 Fracture toughness, K_{Ic}, as a function of applied load, for different waste glasses and for a glass–ceramic.

3.2. Knoop indentations

The average values of b'/a'_2 measured from the Knoop indentations and the H/E values calculated using Equation 3 are given in Table III. Also shown are the estimated values of E based on H and H/E (Knoop) and the average K_{Ic} values evaluated using H/E (Knoop). As can be seen, the estimated values of E are within 15% of the measured E values (Table II), and the fracture toughness calculated using H/E (Knoop) is in close agreement with the value calculated using actual measured values of H/E. The latter observation is obviously due to the rather weak dependence of K_{Ic} on H/E.

3.3. Hertzian indentations

The probability of fracture as a function of load and indenter radius is shown in Fig. 8 for both MCC 76-68 and SM 513 LW 11 waste glasses. Note that both glasses were not tested until after several days exposure to the dry N_2 atmosphere. In the case of the SM 513 LW 11 glass, the initial 7 μm polished surface did not provide a suitable flaw size and density to determine a well-defined load, P_c; therefore, the surface was repolished to a 15-μm diamond finish, which then provided a suitable flaw size and density for determining P_c. These data are shown in Fig. 8. The reason that the MCC 76-68 did not need repolishing may be

TABLE IV Effect of dry nitrogen on K_{Ic} determination

	Vickers indentation				Hertzian indentation	
	K_{Ic} (MN m$^{-3/2}$)				K_{Ic} (MN m$^{-3/2}$)	
Material	Air	N_2, 1 d	N_2, 21 d	N_2, 30 d	N_2, 1 h	N_2, 2 d
MCC 76-68	0.94	0.91	1.05	1.14	–	–
VG 98/12	0.78	0.97	1.07	1.17	–	–
GP 98/12	0.97	0.95	1.17	1.14	1.0	1.08
SM 58 LW 11	1.11	1.10	1.16	1.22	–	–
SM 513 LW 11	1.02	1.15	1.16	1.21	–	–

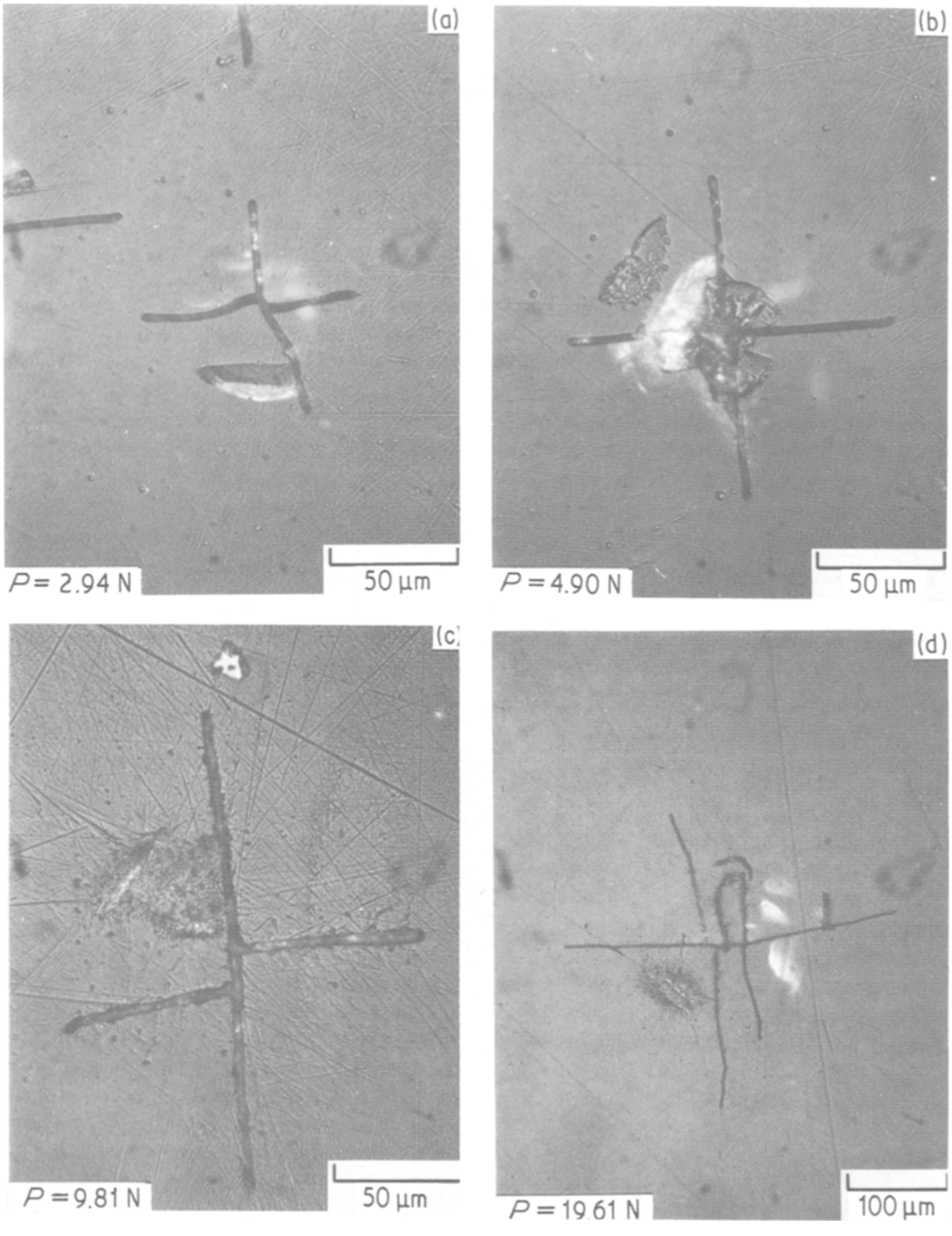

Figure 7 Crack morphology produced by Vickers indentation in the waste glass MCC 76-68, following serial polishing to a depth beyond the indent impression and a short etch (10 min) with HF : H_2O (1 : 10) solution.

the presence of both microscopic pores and metallic inclusions in this material which act as flaws of appropriate size and density. In both glasses, P_c increased linearly with indenter radius, as shown in Fig. 9, indicating that Auerbach's law is obeyed. The indentation parameters and calculated values of γ_F and K_{Ic} are summarized in Table V. The average values of K_{Ic} are 1.13 and 1.23 $MN\,m^{-3/2}$ for MCC 76-68 and SM 513 LW 11, respectively.

TABLE V Indentation parameters and fracture toughness for several waste materials

Material	R (mm)	P_c (N)	r/a_3	$\frac{a_3}{c''}[\phi'']^{-2}$	γ_F ($J\,m^{-2}$)	K_{Ic} ($MN\,m^{-3/2}$)
MCC 76-68	1.5	108	1.30	1350	7.50	1.14
MCC 76-68	2.5	201	1.30	1350	8.38	1.20
MCC 76-68	3.0	216	1.23	1450	6.98	1.10
MCC 76-68	3.5	254	1.19	1500	6.80	1.08
SM 513 LW 11	1.5	141	1.23	1450	8.88	1.30
SM 513 LW 11	3.0	246	1.16	1600	7.02	1.15
GP 98/12	1.5	91	1.26	1400	6.10	1.03
GP 98/12	3.0	160	1.30	1330	5.63	0.99
B1-3*	1.5	202	1.05	3100	3.29	0.85
B1-3*	3.0	450	1.07	2750	4.14	0.95
B1-3*	5.0	780	1.08	2600	4.55	1.00

*Data from [1], but corrected using measured values of ν and E from Table II.

The probabilities for fracture and the critical loads were also previously determined for VG 98/12 [2], GP 98/12 [2], and the B1-3 glass ceramic [1] by Hertzian indentations. However, the reported values of γ_F and K_{Ic} were calculated using assumed values of E and ν, which were smaller than the now-measured values given in Table II. This yielded larger values than expected for both γ_F and K_{Ic}. We have now reassessed the previous data and recalculated γ_F and K_{Ic} using the measured values for E and ν from Table II. In addition, more data were collected, in particular for GP 98/12. The results are also summarized in Table V. Basically, a significant decrease in γ_F and K_{Ic} is caused by the very strong dependence of the crack-extension function, $(a_3/c'')[\phi'']^{-2}$, on ν whenever ν exceeds a value of about 0.2.

4. Discussion

The Vickers indentation technique was used to measure the fracture toughness of several nuclear-waste glasses and yielded very reproducible results, under constant atmospheric conditions, with less than 10% scatter in the data. Several of the waste glasses were also tested by the Hertzian indentation technique; however, this technique is some-

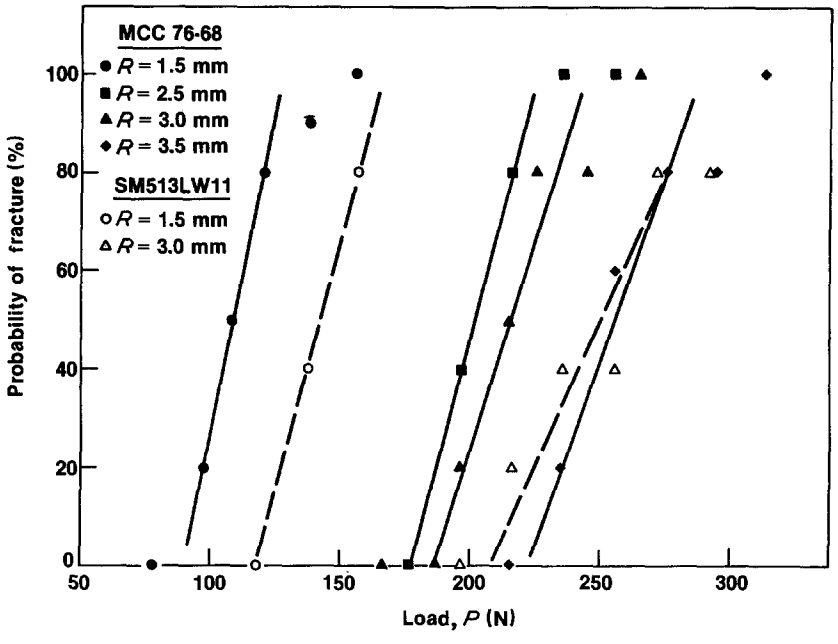

Figure 8 Fracture probability for different indenter radii, R, as a function of applied load, for the two waste glasses MCC 76-68 and SM 513 LW 11.

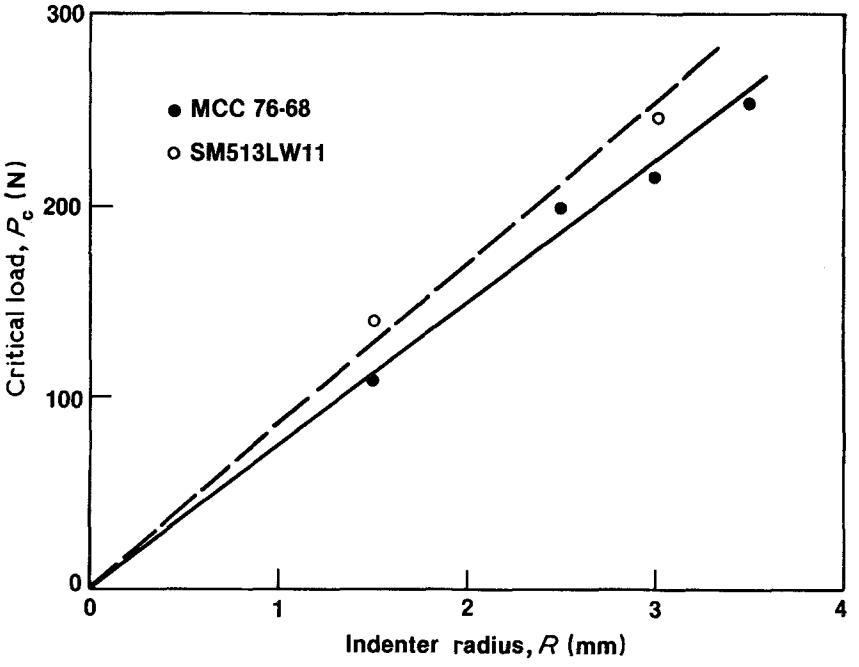

Figure 9 Critical load for Hertzian crack formation, P_c, against indenter radius, R (Auerbach's law), for the two waste glasses MCC 76-68 and SM 513 LW 11.

times sensitive to the pre-existing surface-flaw conditions. The Vickers technique, on the other hand, is independent of the pre-existing surface-flaw conditions [13] and is far less time-consuming than the Hertzian technique, since each indentation yields a value of K_{Ic}. Therefore, the Vickers technique has the potential of yielding a better statistical average with far fewer indentations, making it a very sensitive technique for measuring changes in fracture toughness of nuclear-waste glasses due to process or storage variables.

The partly empirical nature of Equations 1 and 2 raises the question of the accuracy of the calculated value of K_{Ic} based on these equations. As shown in Table VI, the Vickers indentation results agree well with values determined by Hertzian indentation and with the few values determined by the conventional double-torsion method. The

TABLE VI Comparison of K_{Ic} values obtained from different techniques

Material	K_{Ic} (Vickers) ($MN\,m^{-3/2}$)		K_{Ic} (Hertzian) ($MN\,m^{-3/2}$)	K_{Ic} (double-torsion) ($MN\,m^{-3/2}$)
	Air	Dry N_2	Dry N_2	Air
MCC 76-68	0.94	1.14	1.13	0.65‡
VG 98/12	0.78	1.17	1.15*	–
VG 98/12 + Mo	0.78	–	–	–
GP 98/12	0.97	1.14	1.01	0.85‡
GP 98/12 cryst.	0.93	–	–	–
GP 98/26 cryst.	0.99	–	–	–
SM 58 LW 11				
homogeneous	1.11	1.22	1.16†	–
strongly streaked	0.93		0.91†	–
SM 513 LW 11	1.02	1.21	1.23, 1.11‡	0.98‡
B 1-3 glass–ceramic	1.41		0.93	1.33,‡ 0.95§

*Recalculated from new (unpublished) data and original data [2], but using measured values of ν and E (Table II).
†Data from [3].
‡Data from [17], measured in air.
§Data from [20].

slightly higher values observed for the Hertzian data, obtained in the dry-nitrogen atmosphere, may be attributed to the same environmental effect indicated by the results in Table IV. Additional work to resolve the discrepancies in some of the Hertzian data is already in progress.

We have also applied other expressions [9–12] for K_{Ic} to the data. Lankford's expression [9] resulted in larger scatter in the calculated values of K_{Ic}, with a general trend of decreasing K_{Ic} with increasing load (increasing c/a) due to the -1.56 power dependence of c/a in his expression. The data better fits a -1.5 power dependence (as indicated in Fig. 5), which also has at least a theoretical basis. The other expressions [10–12] used to determine K_{Ic} differ primarily in the empirical constant of Equation 2; however, on the basis of the present work no change from the original expression used can be suggested.

As was shown in Fig. 7, the crack morphology produced by the Vickers indentations in the glasses of this study are suggested to be half-penny shaped and not of the Palmqvist type. This agrees well with the observed $P^{2/3}$ dependence of the crack length c (Fig. 5), since it is generally observed [21] that for half-penny cracks c follows a $P^{2/3}$ dependence whereas for Palmqvist cracks c is linearly dependent on P. Lankford [9, 22], however, has observed a $P^{2/3}$ dependence of c for several materials in which he proposes that the cracking is of the Palmqvist type; therefore, the $P^{2/3}$ dependence of c may not always accurately reflect crack morphology. Both Lankford [22] and Haronah *et al.* [13] have suggested that the half-penny cracks observed in glasses are initiated by surface radial cracks rather than median cracks. On the basis of the crack patterns observed by serial polishing in this study (Fig. 7), it cannot be concluded whether the observed half-penny cracks are median- or radial-initiated; however, it is interesting to note that, at all the loads investigated, one of the half-penny cracks appeared continuous below the indenter impression (see Fig. 7), while the other half-penny crack generally exhibited a slight offset (or ledge) on each side of the continuous half-penny crack. The interpretation is not clear, but suggests that a half-penny crack may actually be formed by the merging of two radial cracks, as suggested by Lankford [22] and Haranoh *et al.* [13].

All the waste glasses, including those with fine crystallized products, have fracture-toughness values in air of the order of 0.9 to 1.1 MN m$^{-3/2}$. This very narrow range of values agrees with the observations of Vernaz *et al.* [23] and suggests that minor variations in the waste glass composition do not significantly affect fracture toughness. The exceptions are the VG 98/12 and VG 98/12 + Mo glasses which show significantly lower values of K_{Ic} when measured in air by Vickers indentation. These two glasses are apparently more susceptible to environmental effects than the waste glasses containing fission products. When comparing results, the influence of the environment on K_{Ic} should always be considered. The presence of humidity (or water) causes K_{Ic} to decrease, both with the present and with other materials (e.g. [11, 24, 25]); therefore, testing in a controlled atmosphere (dry N_2) might be preferred. The data on GP 98/12 and SM 58 LW 11 in Tables III and VI also suggest that partial crystallization might decrease the fracture toughness slightly.

The Bl-3 glass ceramic is the only material tested in this study which was not well-behaved under Vickers indentations. As shown in Fig. 6, the calculated fracture-toughness values show considerable scatter, which was not observed in the hardness values (Fig. 4). The scatter in the data is due primarily to the presence of the very coarse crystalline material in the glass–ceramic matrix. These crystals inhibit crack propagation to some extent or, in some instances, abruptly terminate the cracks. Thus the effective value of c is decreased, causing a scattered increase in K_{Ic}. The Hertzian technique, on the other hand, yields a less scattered and lower value of the fracture toughness. Since the Hertzian cracks propagate in a circular pattern, the measurements are less affected by the presence of large crystalline phases and yield a fracture toughness value that is, perhaps, more representative of the bulk material. It is expected that more measurements (increased statistics) might better define the K_{Ic} value from Vickers indentations, but for other coarse multiphase materials, such as the waste form Synroc [26], the Hertzian technique can be expected to yield better results.

The Knoop indentation test proposed by Marshall *et al.* [14] has proven to be a valuable method for determining the H/E ratio. The K_{Ic} values calculated using the H/E (Knoop) value are within 5% of those calculated using the measured values of H and E. Also, from the measured value of H and the H/E determined by Knoop indentations, Young's modulus, E, can be determined to within

15%. Therefore, the combination of Vickers and Knoop indentations can yield values of K_{Ic}, H, and H/E (or E).

5. Summary

The fracture toughness of several nuclear-waste glasses and of a nuclear-waste glass ceramic were measured by indentation techniques. The Vickers indentation technique proved to be a very reliable method for nuclear-waste glasses and far less time-consuming than the Hertzian technique. While the Vickers technique was independent of the pre-existing surface-flaw condition, the Hertzian technique proved to be somewhat sensitive to the surface flaws. Both techniques, however, give results for waste glasses that were in good agreement with each other and with the results of double torsion. In the case of the coarse glass ceramic, the Vickers technique was less satisfactory, while the Hertzian technique proved reliable and may be preferred for coarse multi-phase materials. In all cases, the presence of water (humid air) decreased the measured values of K_{Ic}; therefore, testing in a controlled atmosphere may be preferred.

The Knoop indentation test for determining the ratio, H/E, of nuclear-waste glasses yielded values that agree quite well (within 15%) with values determined from H and E measured by conventional methods. The H/E values obtained by Knoop indentation did not significantly affect the determination of K_{Ic} (within 5%) and could also provide a relatively good estimate of E (within 15%) if H is also measured or known. Therefore, the combination of Vickers and Knoop indentations can yield, for waste glasses, values of K_{Ic}, H and H/E (or E).

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