CERAMIC FILTERS

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ABSTRACT

Filters were formed from ceramic fibers, organic fibers, and a ceramic bond phase
using a papermaking technique. The distribution of particulate ceramic bond phase
was determined using a model silicon carbide system. As the ceramic fiber
increased in length and diameter the distance between particles decreased. The
calculated number of particles per area showed good agreement with the observed
value. After firing, the papers were characterized using a biaxial load test. The
strength of papers was proportional to the amount of bond phase included in the
paper. All samples exhibited strain-tolerant behavior.

Keywords: ceramic fiber; filter; papermaking

INTRODUCTION

Fibrous filters have been used for centuries to protect individuals from dust, pathogens
disease, smoke, and other gases or particulates [1]. In the 1970s and 1980s
ceramic filters were developed for filtration of hot exhaust gases from diesel
engines[2-4]. Tubular, or candle, filters have been made to remove particles from
gases in pressurized fluidized-bed combustion and gasification-combined-cycle
power plants [5]. Very efficient filtration is necessary in power plants to protect the
turbine blades. The limited lifespan of ceramic candle filters has been a major
obstacle in their development.

The present work is focused on forming fibrous ceramic filters using a
papermaking technique. These filters are highly porous and therefore very
lightweight. The papermaking process consists of filtering a slurry of ceramic
fibers through a steel screen to form paper. Papermaking and the selection of
materials will be discussed, as well as preliminary results describing the geometry
of papers and relative strengths.

EXPERIMENTAL

Four classes of materials were used in making ceramic filters. These were the

ceramic fiber, an organic binder fiber to hold the paper together and provide strength before firing, a bulking fiber to maintain an open, porous structure, and the ceramic bond phase. The ceramic fibers evaluated were Saffil®, Nextel 312®, fused quartz fibers (QPC 300® and QPC 125®), fiberglass, and two aluminosilicate fibers with alumina to silica ratios of 60%:40% and 87%:13%. The composition, diameter, and use temperature of the ceramic fibers are summarized in Table I. The QPC quartz fibers were heated to remove sizing prior to paper forming. All fibers were used in chopped form.

Table I. Summary of Ceramic Fibers

Fiber	Composition	Diameter	Continuous Use Temp (°C)	Manufacturer
Saffil®	Al_2O_3	3 micron diam.	1600	ICI
Nextel 312®	62% Al_2O_3: 24% SiO_2: 14% $B2O3$	10 - 12 micron diam.	1200	3M
QPC 300®	SiO_2	9 micron diam. (3 mm long)	1000	Quartz Products Company
QPC 125®	SiO_2	14 micron diam. (13 mm long)	1000	Quartz Products Company
Al_2O_3:SiO_2	60% Al_2O_3: 40% SiO_2	20 micron diam.	1300	Zircar
Al_2O_3:SiO_2	87% Al_2O_3: 13% SiO_2	8 micron diam.	1600	Zircar
Fiberglass	SiO_2	33 micron diam.	400	Zircar

Polyethylene[†], polyester[§], polypropylene[‡], cellulose acetate[¤], cellulose[#], and fibrillated acrylic[¶] were tested as binder fibers. Cellulose[*] and Crestbrook pine[+] were examined as bulking fiber. Colloidal silica[◊] and four particulate alkali glasses[¥] were used for ceramic bond phase.[♭] Table II summarizes selected properties of the glasses. The sintering temperature[♭] of the colloidal silica was experimentally determined to be 1200°C.

The ceramic filters were formed using a papermaking technique. It was determined that 9 grams of fibers were sufficient to form a paper approximately 20 cm x 20 cm

x 0.1 cm. The total fiber weight was comprised of 75% ceramic fiber, 15% binder fiber, and 10% bulking fiber. The fibers were mixed in a blender in one liter of water. This slurry was poured into a Williams Standard Handsheet Mold** (Figure 1) and further diluted with water to a volume of 5 liters. Upon draining the water from the handsheet mold, the fibers formed a paper on a stainless steel screen. This

Table II. Glass Bond Phases

Glass	Composition	Diameter	Softening Temp. (°C)	Sintering Temp. (°C)
7052	Alkali Barium Borosilicate	9.4 micron	712	770
7056	Alkali Borosilicate	7.6 micron	718	770
7070	Lithia Potash Borosilicate	17.0 micron	Not Available	770
9013	Alkali Barium	10.7 micron	656	670

paper could be easily removed from the screen and handled after drying. Ceramic bond phase was incorporated into the paper either by direct addition to the slurry or by dip coating the dried paper in a suspension of bond phase in water.

Comparison of papers formed with the various ceramic fibers and binder fibers was accomplished by determining the average relative strength of papers in tensile tests. Strips of paper 2.5 cm x 0.6 cm (1 inch x 0.25 inch) were loaded axially along the length of the sample to determine the breaking strength of the paper. Results from this test were used to select model systems for further study. Once ceramic fibers and binder fibers were chosen, the ceramic bond phases were compared using a biaxial loading test. Discs 5.8 cm (2.3 inch) in diameter were cut from fired ~~placed~~ papers. These discs were placed on a supporting ring of the same diameter, a load was applied in the center of the disc at 7.9 x 10^{-3} cm/minute (0.02 inch/minute), and the breaking load and displacement were recorded. In this way, the different ceramic bond phases could be compared, and the amount of bond phase necessary to obtain acceptable strength could be evaluated.

RESULTS AND DISCUSSION

Fiber Evaluation

The relative strength of papers made with the different binder fibers was measured for papers which included Saffil® as the ceramic fiber and cellulose as the bulking fiber. The results are shown in Figure 2. Papers formed with the acrylic fiber were significantly stronger in tension than papers made with the other binder fibers. The

acrylic fiber is highly branched, or fibrillated, with large numbers of long fibrils. These fibrils are very efficient at mechanically bonding particles or other fibers. The acrylic was the only one of the binder fibers tested which was fibrillated. Its high degree of fibrillation makes this fiber an excellent binder fiber for paper.

A similar test was conducted to select appropriate ceramic fibers. The results obtained from as formed, unfired papers made with cellulose acetate binder fiber and cellulose bulking fiber are provided in Figure 3. The goal of this test was to make a filter similar to Whatman® analytical filters, and therefore strength alone was not a sufficient criterion to determine which ceramic fibers to study. Qualitative criteria such as brittleness, ease of tearing, the ability to be folded and hold a pleat, and ease of handling were noted and are summarized in Table III. Fiberglass filters proved to be the strongest samples, however papers containing this fiber were very brittle and difficult to handle. The two aluminosilicates performed well in the tensile test, yet resulted in very thin papers which tore easily when removed from the stainless steel screen. Papers made from the Saffil®, Nextel 312®, and quartz (QPC®) fibers were similar in relative strength. Papers made with Nextel 312® ceramic fibers were susceptible to tearing and showed no ability to fold or be formed into simple shapes such as pleats. The Saffil® and QPC 300® fibers resulted in the most satisfactory papers overall, based on the criteria in Figure 3 and Table III, and were selected as the ceramic fibers to study further.

Table III. Summary of Papers Made with Various Ceramic Fibers

Ceramic Fiber	Brittleness	Ability to Fold	Ease of Tearing	Ease of Handling
Saffil®	not brittle	very good	high	excellent
Nextel 312®	not brittle	poor	low	very good
QPC 300®	not brittle	very good	high	excellent
Al_2O_3:SiO_2 (60%:40%)	not brittle	very good	high	poor
Al_2O_3:SiO_2 (87%:13%)	not brittle	very good	high	poor
Fiberglass	very brittle	poor	low	moderate
Whatman® filter	not brittle	very good	low	excellent

Bond Phase Particle Capture

One method of incorporating the particulate ceramic bond phase into the paper is to add it to the fiber slurry before the paper is formed. When using this method, it is desirable to know the distribution of the particles in the paper. To model the

distribution of particulate glass bond phase, one gram of silicon carbide particles of known size was used. The black silicon carbide particles were easily seen under an optical microscope, as opposed to the white glass particles. The silicon carbide particles could be counted to determine the number of particles per area of paper as a function of particle size and the specific region of the paper being studied, i.e. the center or the edge. Silicon carbide particles of 14.5, 23, and 50 micron diameter were used. Using an optical microscope, the number of particles observed in a known area were counted. A hole punch was used to remove samples from the outer edge and middle of the paper. Observations were made on both the top and bottom surfaces of each sample. Specimens were then peeled apart to make observations on the inside of the paper.

When Saffil® was used as the ceramic fiber the distribution of particles showed some dependence on the particle size. In these instances, the 50 micron silicon carbide particles were more numerous in the middle of the paper than along the edge, while the opposite was true of 14.5 micron particles. The 23 micron particles resulted in the most uniform distribution between the edge and middle of the paper. When QPC 300® fibers were used the particle distribution was much more uniform across the paper, independent of the particle size used. For all samples, it was observed that more particles were captured in the inner layers of the papers than the outer surfaces, independent of the ceramic fiber used.

The average number of particles per area for several papers is shown in Figure 4. Blends of QPC 300® and QPC 125® (80%:20% and 50%:50%) were used to study the effect of fiber length (Table I) in particulate bond phase capture. As seen in Figure 4, the QPC® fibers were slightly more efficient at capturing bond phase than the smaller Saffil® fibers. More small particles (14.5 and 23 micron) were captured in papers made of QPC 125® ceramic fiber than QPC 300®. The papers studied to obtain the results in Figure 4 contained fibrillated acrylic binder fiber and Crestbrook pine bulking fiber. As discussed previously, the fibrillation of the acrylic makes this fiber very efficient at capturing particles. To determine the particle capture caused only by the ceramic fibers and remove any effect due to the fibrillated acrylic, the experiment was repeated with papers which did not contain acrylic fiber. These papers retained only two particles/mm^2, regardless of the ceramic fiber used. To determine how much bond phase was present in a paper which was formed with acrylic, and subsequently subjected to binder burnout, the papers used in Figure 4 were heated to 800°C and the silicon carbide particles recounted. When compared to the data in Figure 4, no significant change in the number of particles present was noted.

Initial Model of Ceramic Filter Paper

Preliminary calculations were made to begin development of a model to describe the geometry of the filter papers. Using known quantities such as the dimensions of the papers, the amount and density of ceramic fibers used, and the amount and density of silicon carbide used, several properties of the papers were calculated. While the detailed calculations are not reported here, the results are summarized in

Table IV. All the values in Table IV were determined based on 23 micron silicon carbide particles as model ceramic bond phase. The observed particle per area values listed in Table IV were acquired from papers containing 23 micron silicon carbide. Good agreement was found for the calculated and observed numbers of particles per mm². *— what constitutes "good agreement?"* *?*

Table IV. Properties of Paper

Ceramic Fiber	% Porosity	Length Ceramic Fiber@	Particle/ Length	Particle/ Area	Observed Particle/Area
Saffil®	94.8	84.8 km	0.58/mm	3.2/mm²	8/mm²
QPC 300®	93.3	48.7 km	1/mm	9.5/mm²	11/mm²
QPC 125®	93.3	20 km	2.45/mm	14.9/mm²	38/mm²

@ length of fiber in 20 cm x 20 cm x 0.1 cm paper

Calculated

Biaxial Load Test

Samples from fired papers containing one of four ceramic bond phases were tested using a biaxial load test. Glass bond phases 7052, 7056, and 9013 were added to slurries of Saffil® paper in 5 and 10 gram quantities. The colloidal silica bond phase was incorporated into papers by dipping Saffil® papers in 5%, 10%, or 30% aqueous colloidal silica solutions prior to firing. These papers contained approximately 0.4 g, 0.7 g, and 2.2 g of silica, respectively. The relative breaking loads for all samples are presented in Figure 5. Papers containing 5 grams of 7052 glass bond phase were half as strong as papers containing 10 grams of 7052. The relative strengths of papers containing colloidal silica increased in the ratio 1:3:6.5 as the amount of silica in the paper increased in the ratio 1:2:6. These examples indicate that increasing the amount of bond phase results in an increase in the number of bonds between fibers in the paper, thereby increasing the strength of the paper proportionally. The strength of papers made with 7056 and 9013 glass bond phases did not increase with the amount of bond phase added. This could be due to insufficient wetting of the bond phase on the fibers, possibly caused by surface chemistry problems or a firing temperature which was not high enough. The displacement observed during loading was approximately 50% greater for the papers made with glass bond phase than for those made with colloidal silica. Papers made with glass or colloidal silica bond phase showed strain-tolerant behavior during testing, and exhibited graceful rather than catastrophic failure. A plot representative of the failure behavior of all the papers is presented in Figure 6.

SUMMARY

Filter papers were made using Saffil® and fused quartz ceramic fibers, acrylic binder fibers, bulking fiber, and ceramic bond phase. The fibers used were selected by tensile testing of papers made with several different ceramic and organic fibers. Glass and colloidal silica were used as the ceramic bond phase and were incorporated into the papers by addition to the fiber slurry or by dip coating prior to firing. Firing temperatures were determined experimentally. Silicon carbide particles of known size were used to model the distribution of particulate bond phase in the papers. The number of particles in a known area were counted under an optical microscope. More particles were captured in the inner layers of paper than the top or bottom surfaces. The particle distribution in the edge and center of the papers showed some dependence on particle size. As the ceramic fiber increased in length and diameter the calculated distance between particles decreased. The calculated number of particles per mm^2 showed good agreement with the observed number of particles per mm^2. Fired papers were subjected to biaxial load tests. The strength of papers made with 7052 glass and colloidal silica showed a dependence on the amount of bond phase included in the paper. All samples exhibited strain-tolerant behavior.

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† Polyethylene, Dupont Co., Wilmington, DE
§ Polyester, Schuller International, Denver, CO
‡ Polypropylene, Hercules, Passaic, NJ
¤ Cellulose Acetate, Hoescht-Celanese, Somerville, NJ
Cellulose (high alpha), Rayonier, Stamford, CT
¶ Fibrillated Acrylic (114-3), Cytec Industries Inc., Stamford, CT
* Kimwipe, Kimberly-Clark Corp., Roswell, GA
+ Crestbrook pine pulp, Buckeye Cellulose Corp., Memphis, TN
◊ Colloidal Silica, Matheson, Coleman, and Bell, Cincinnati, OH
¥ Sealing Glasses, Corning, Corning, NY
** Williams Standard Handsheet Mold, Testing Machines Inc., Amityville, NY

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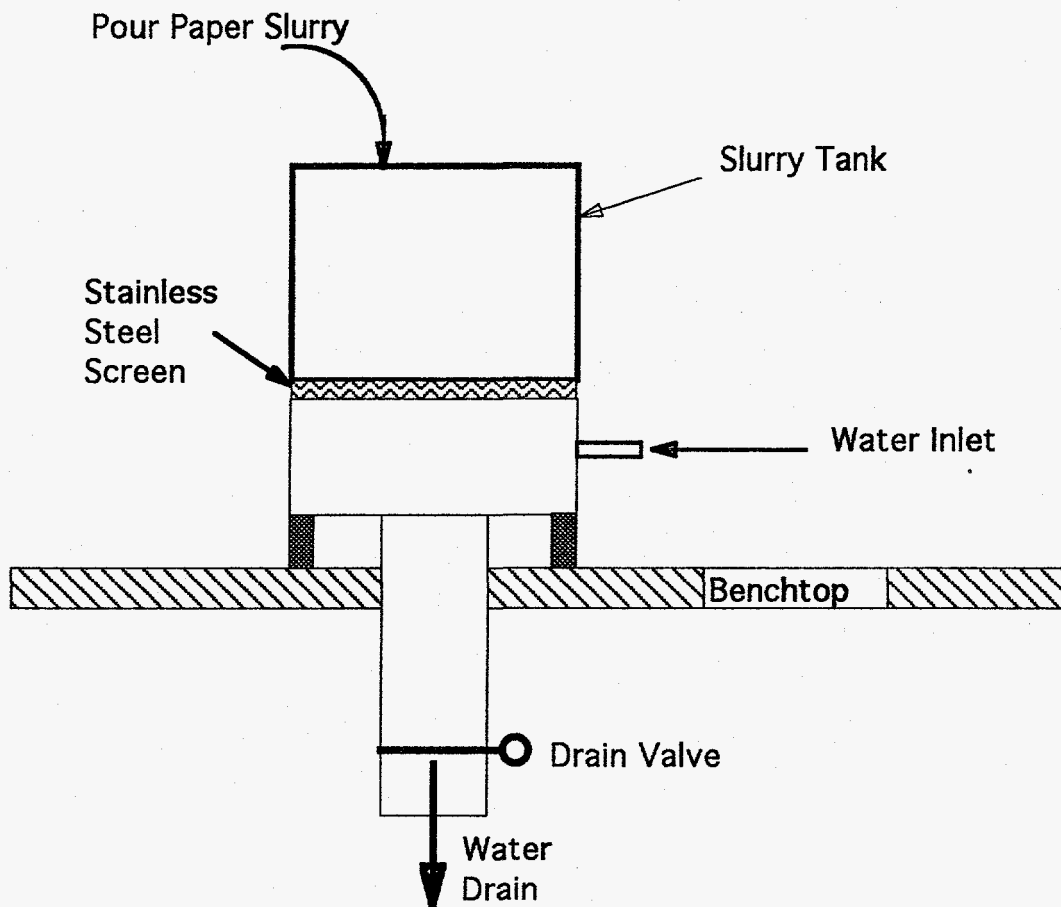
Pour Paper Slurry

Slurry Tank

Stainless
Steel
Screen

Water Inlet

Benchtop

Drain Valve

Water
Drain

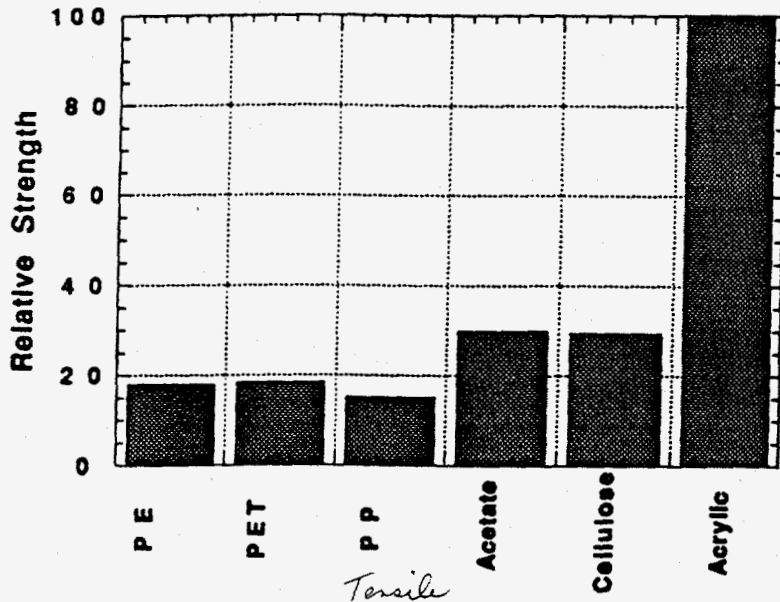**Figure 1: Williams Standard Handsheet Mold**

Figure 2: Relative Strengths of Binder Fibers
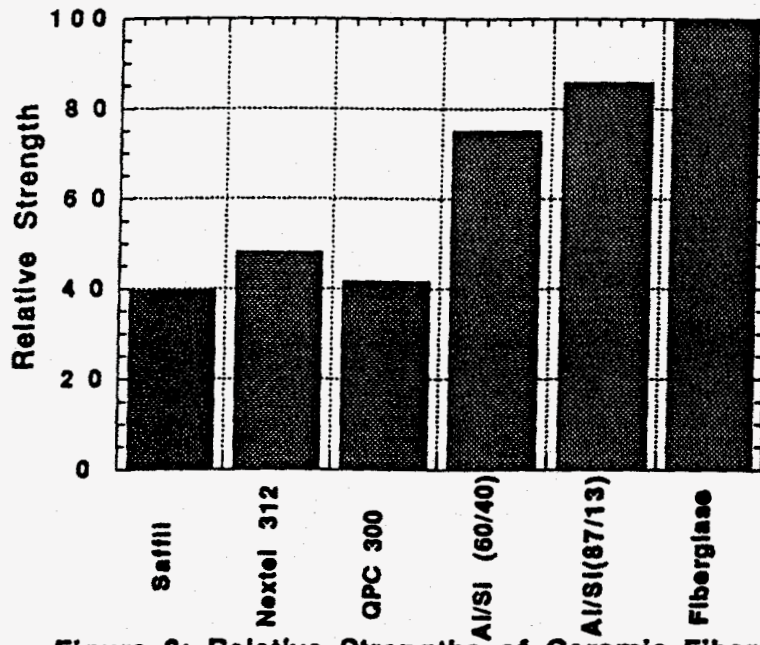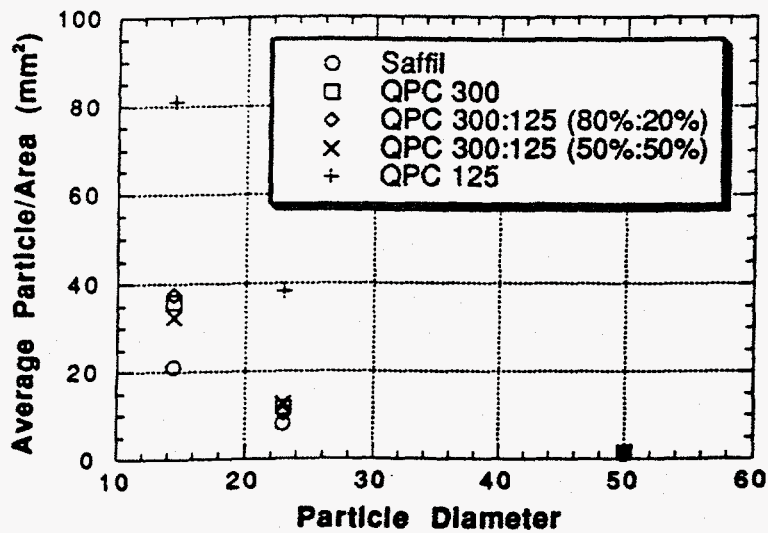

Figure 3: Relative Strengths of Ceramic Fibers
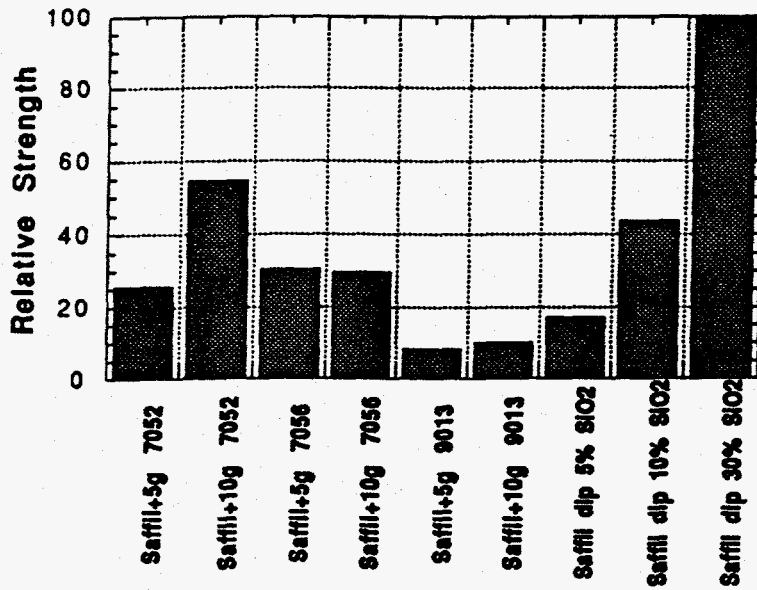
Figure 4: Particulate Bond Phase/Area

Figure 5: Relative Compression Strength of Fired Papers
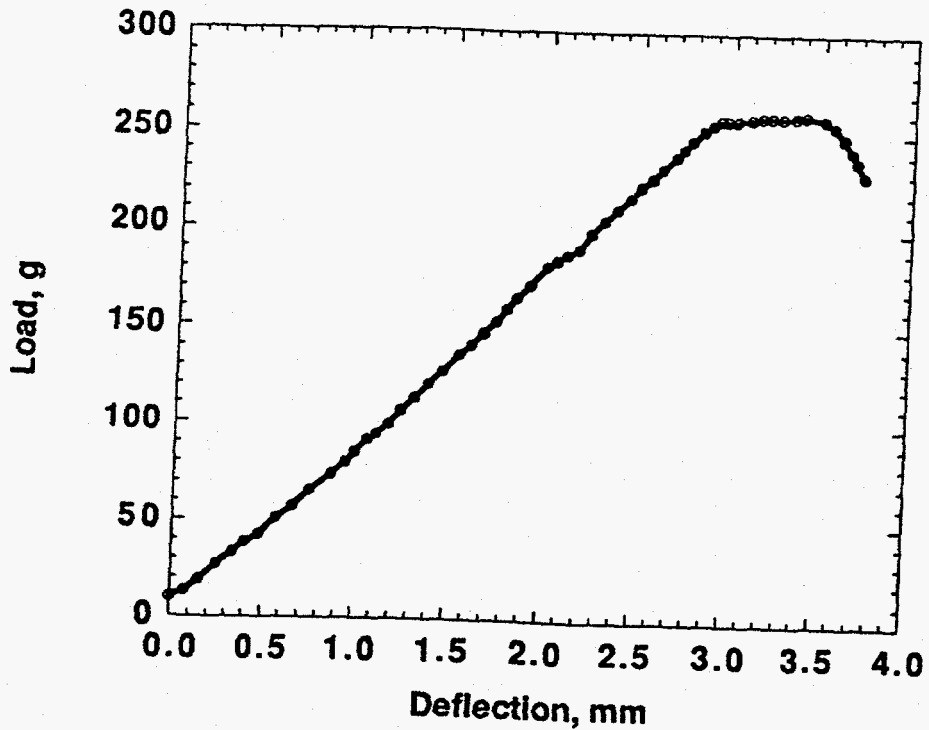
Figure 6: Filter Paper Strain-Tolerant Behavior During Mechanical Testing