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Improving an alumina fiber filter membrane for hot gas filtration using an acid phosphate binder

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Alumina fiber based filter membranes were prepared using acid phosphate (phosphoric acid plus aluminum hydroxide), colloidal alumina, monoaluminum phosphate and three types of colloidal silica binders at various binders contents. The filter membranes containing between 5% and 10% by weight of acid phosphate binder exhibited the highest flexural strength, compressive strength, work of fracture and elastic modulus in comparison to those containing the other binders at equivalent binder contents, and exhibited the lowest pressure drop in comparison to membranes with other binders and having equivalent flexural and compressive strengths. Microscopy showed that the acid phosphate caused the fibers to bond at their junctions only, whereas colloidal alumina or colloidal silica binders caused free binder particles within the fiber network.

1. Introduction

A potential application for ceramic membrane filters is the cleaning of exhaust gases from coal fired power stations. A key requirement for this application is the capability to withstand high temperatures and reducing environments for prolonged periods. However, the use of ceramic filter membranes for high temperature gas filtration applications is often limited by their susceptibility to brittle failure and lower strength compared to competing technologies.

Previous work has recommended that aluminosilicates such as mullite and cordierite or alumina, titania and silicon carbide would be good candidate materials for the manufacture of ceramic membrane filters [1]. Even though the binder usually constitutes only a small percentage of the filtration medium, the binder system used in the ceramic membrane filter is critical to the mechanical properties and filtrate flow characteristics. However, little attention has been given to evaluating various binder systems in an effort to optimize the desired properties, namely, pressure drop across the filter membrane and mechanical properties.

Silica is a widely used binder in the refractory and ceramic industry [2]. It is often used in the form of an aqueous dispersion containing 20 to 50% by weight of silica particles. The average size of the silica particle can range from under 10 nm to over 80 nm. The silica binder has many advantages, including its ease of use. However, silica does have some disadvantages that are especially important when considering its use for filtration applications. One such disadvantage is its tendency to fill the open or continuous porosity of the filter membrane. Colloidal alumina is also used in high temperature refractory applications where colloidal silica binders fail because of their temperature limitation. The alumina binder has the advantage of being a higher temperature material and would be ideal when used with alumina fiber since there would be no mismatch of the coefficient of thermal expansion. However, since colloidal alumina is also a particulate binding medium, it will have the same undesirable effect of filling the open porosity of the filter membrane.

Phosphate has also been utilized as a binder in the refractory industry for many years and details of the reactions are given in the literature [2, 3]. There are several types of phosphate binders that are used with ceramic materials. Pirogov *et al*. [4] used an orthophosphoric acid (H_3PO_4) binder in a mullite-corundum body in their study to determine the optimum content of graphite and SiC additives. Birchall *et al*. [5] studied the mechanical properties of an unsintered SiC compact bonded by aluminum phosphate ($AlPO_4$) glass. Toy and Whittemore [6] evaluated the reactivities of several calcined aluminas with orthophosphoric acid and demonstrated that a glassy $AlPO_4$ phase and aluminum metaphosphate ($Al(PO_3)_3$) are effective bonding phases. Phosphoric acid has also been shown to be effective for bonding refractory castables composed of sintered aluminum oxide [7]. These castables are characterized by high bond strength and very high resistance to erosion over a wide temperature range. Monoaluminum phosphate ($Al(H_2PO_4)_3$) and magnesium phosphate ($Mg(H_2PO_4)_2$) are also reported to be suitable for use in refractory and ceramic foam applications [2].

Gitzen *et al*. [7] outlined the three methods of using phosphate bonding in refractory materials: (1) the use of siliceous materials with phosphoric acid; (2) the use of oxides with phosphoric acid; and (3) the direct addition or formation of an acid phosphate. The addition of aluminum significantly increases the bonding

capability of acid phosphates [3]. Chiou and Chung [2] developed aluminum phosphate binders with various P/Al atom ratios and demonstrated that a P/Al ratio of 23 resulted in the highest bonding strength when used with SiC whiskers and short carbon fibers. The aluminum phosphate binders developed by Chiou and Chung were called acid phosphates because they contained phosphoric acid in excess of what is needed to form aluminum phosphate.

This paper evaluates and compares the performance of an alumina fiber based filter membranes using colloidal alumina, monoaluminum phosphate, three types of colloidal silica and an acid phosphate binder developed by Chiou and Chung [2].

2. Experimental methods

2.1. Membrane filter medium

An alumina (Al_2O_3) fiber (Table I) was used as the membrane filter medium.

2.2. Binders

Three types of colloidal silica were used in this study. The first type of colloidal silica, having a grade designation of Ludox HS40, was obtained from DuPont Chemicals (Wilmington, Delaware). This grade of colloidal silica has a silica particle diameter of 12 nm and a surface area of 220 m^2/g. The second type, Nalco 2329, was obtained from Nalco Corporation (Chicago, Illinois). Nalco 2329 has a silica particle diameter of 75 nm and a surface area of 40 m^2/g. The third type, Megasol S50, was obtained from Wesbond Corporation (Wilmington, Delaware). Unlike the above mentioned types of colloidal silica, Megasol S50 has a size distribution of silica particles with an average particle size of approximately 70 nm and a surface area of 70 m^2/g. The colloidal alumina, having a grade designation of Nyacol AL-20, was obtained from PQ Corporation (Valley Forge, Pennsylvania). It has a particle size of 50 nm and a solids content of 20 wt%. The monoaluminum phosphate, having a grade designation of Ref-Bond BMAP, was obtained from Refractory Minerals Company, Inc. (Unionville, Pennsylvania). Details of the commercially available binders are outlined in Table II.

TABLE I Properties of Al_2O_3 fiber

Manufacturer	ICI performance chemicals
Trade name	Saffil
Grade	RF milled
Mean diameter (μm)	3[a]
Density	3.3[a]
Tensile strength (MPa)	2.17[b]
Crystal structure	>2000[a]
Melting point (°C)	δ alumina[a]

[a]From Ref. 3.
[b]From Ref. 4.

A non-commercial phosphate binder solution was prepared by mixing one part aluminum hydroxide ($Al(OH)_3$, obtained from Aldrich Chemical Co., Milwaukee, Wisconsin) with phosphoric acid (H_3PO_4, 85% Technical Grade, also obtained from Aldrich Chemical Co), such that the solution had a P/Al atom ratio of 23 [2, 10]. The phosphoric acid was stirred and heated to approximately 150°C. Then aluminum hydroxide was slowly mixed in and allowed to dissolve completely. As done by Chiou and Chung [2, 10] and Lai and Chung [11], this binder was denoted by AP23.

2.3. Membrane filter fabrication

Alumina fiber filter membranes with the AP23 binder were fabricated using a wet forming method. To attain a binder content of 9 to 9.5 wt%, the AP23 binder was added to water with a ratio of 1 part binder to 15 parts of water, followed by the addition of the fiber. For making filter membranes with a lower binder content, more water was used. The slurry was passed through a cylindrical forming mold with a stainless steel screen (200 mesh) at the bottom and a wet cake was formed. A small amount of vacuum was used to aid in draining the binder/water mixture from the filter membrane. The filter membrane was then dried and heat treated at 800°C for 3 h.

The colloidal alumina, colloidal silica and monoaluminum phosphate binder containing filter membranes were also fabricated using the same wet forming method. As with the AP23 acid phosphate binder, all the filter membranes were put through a heat treatment step of 800°C for 3 h. It has been shown by Chiou and Chung [10] and others [11, 12] that this heat treatment time-temperature regimen is effective for the AP23 binder as well as the colloidal silica, monoaluminum phosphate and colloidal alumina binders in activating their binding capability.

2.4. Membrane filter characterization

Characterization of the membranes was related to properties important to the potential application of hot gas cleaning. The properties included pore structure, pressure drop and mechanical properties.

TABLE II Properties of commercial binders used in this work

Property	Silica (Ludox HS40)	Silica (Nalco 2329)	Silica (Megasol S50)	Alumina	Monoaluminum phosphate
Particle diameter (nm)	12	75	70 average	50	–
Specific surface area (m^2/g)	220	40	70	–	–
pH	9.7	8.4	9.0–9.5	4.0	1.0–1.6
Specific gravity	1.31	1.29	1.39	1.19	1.70–1.76
Solids content (wt%)	40	40	50	20	55.5
Viscosity @ 25°C (cPs)	16	10	15	10	2000

2.4.1. Pore structure

The pore structure for the different binders and binder amounts was characterized using scanning electron microscopy.

2.4.2. Mechanical properties

The flexural strength of the filter membranes were measured using rectangular bar specimens in a three-point bending mode. The specimens were cut using a diamond saw and the surfaces polished using a 400 grade SiC grinding paper. The final dimensions were 50 mm × 8 mm × 6 mm. A loading span of 40 mm and a crosshead speed of 0.1 cm/min was used for the test. Fig. 1 illustrates the typical load-displacement curve for a fiber filter membrane. It is clear that the mode of failure was gradual and not typical of a high density brittle ceramic material. The flexural strength and elastic modulus was calculated using the following equations:

$$\sigma_f = \frac{3PL}{2bh^2} \tag{1}$$

$$E = \frac{PL^3}{12bh^3 y_{\max}} \tag{2}$$

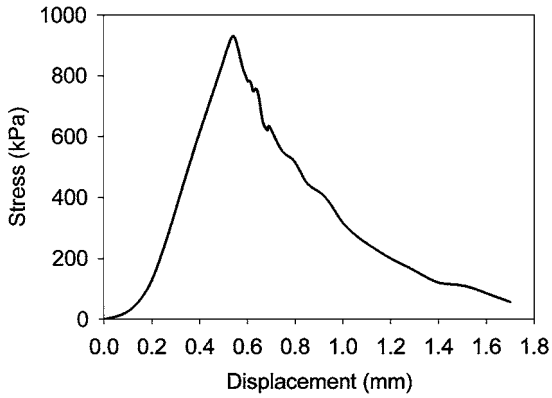

Figure 1 Typical stress-displacement curve during flexural testing.

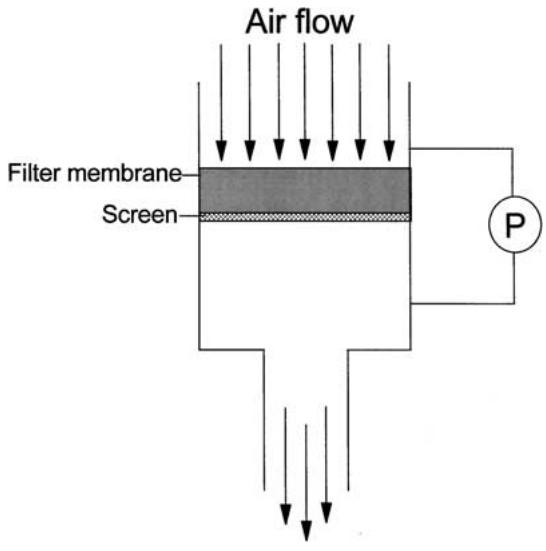

Figure 2 Schematic illustrating the apparatus used to measure the pressure drop across the filter membrane. *P* refers to a pressure gage.

where P is the maximum load, L is the loading span, b is the width of the specimen, h is the height of the specimen, and $y_{\max}$ is the deflection.

2.4.3. Pressure drop

A schematic shown in Fig. 2 illustrates how the pressure drop was measured for the ceramic fiber filter membranes. The filter membranes used in this study were 75 mm in diameter and 10 mm in thickness.

3. Results and discussion

3.1. Pore structure

Fig. 3 shows a scanning electron micrograph of the silica binder used with the alumina fiber. It is evident from the micrograph that there is a considerable amount of free silica that is not contributing to the binding of the fibers and therefore not contributing to the strength of the filter membrane.

Fig. 4 shows the colloidal alumina used with the alumina fiber. It is evident from this micrograph that there is also a considerable amount of colloidal alumina binder that is not contributing to the binding of the alumina fiber. This explains the lower flexural and compressive strength (Sec. 3.2) of the filter membranes made with the colloidal alumina.

Fig. 5 shows a scanning electron micrograph of a filter membrane with the AP23 binder at 9.5 wt%. The effective action of the binder is seen in the open structure formed by alumina fiber and the AP23 binder. The binder causes bonding at the junctions of two or more fibers and forms a porous structure that has little binder that is not contributing to the strength of the fiber structure (Fig. 6).

3.2. Mechanical properties

Fig. 7 shows the increase in flexural strength of the filter membranes when using the AP23 binder at 9 to 9.5% binder content. At levels of binder between 5 and 10 wt%, the AP23 binder gives higher flexural strength than all the other binders. It is possible to get increased flexural strength with the other binder systems, but considerably more binder is needed to achieve the same flexural strength.

Fig. 8 shows the compressive strength of the filter membranes made using the different binders. The compressive strength also shows an improvement when using the AP23 binder compared to the colloidal silica, colloidal alumina and monoaluminum phosphate at the same binder content.

The work of fracture was also calculated from the flexural testing data. The work of fracture (W) was determined by dividing the area (U) under the load vs. displacement curve by the fracture surface area, which is twice the projected area of one fracture surface (A) [13].

$$W = \frac{U}{2A} \tag{3}$$

As expected, the work of fracture for the AP23 binder in comparison to those for the other binders is similar

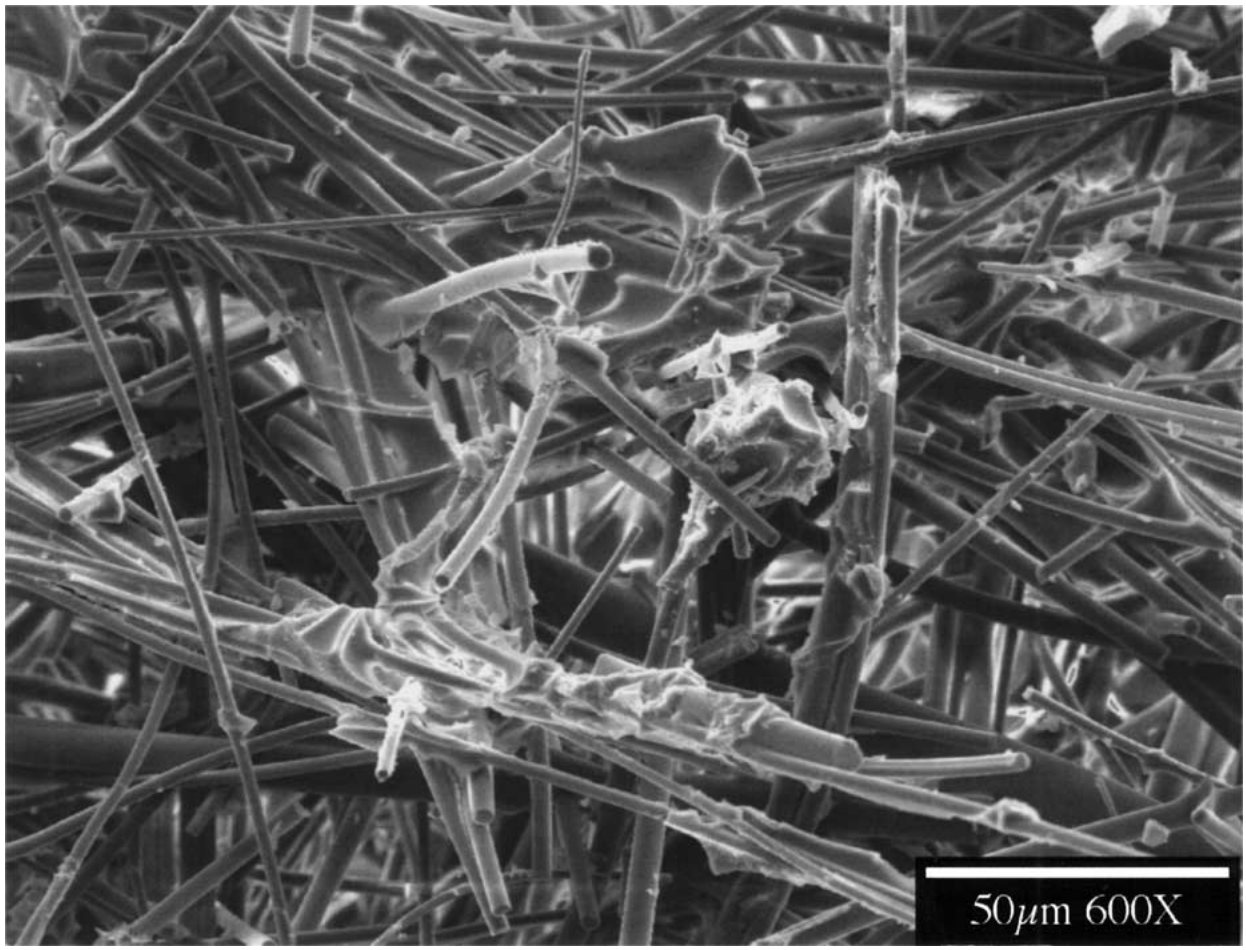

Figure 3 Scanning electron micrograph of a filter membrane with colloidal silica binder.

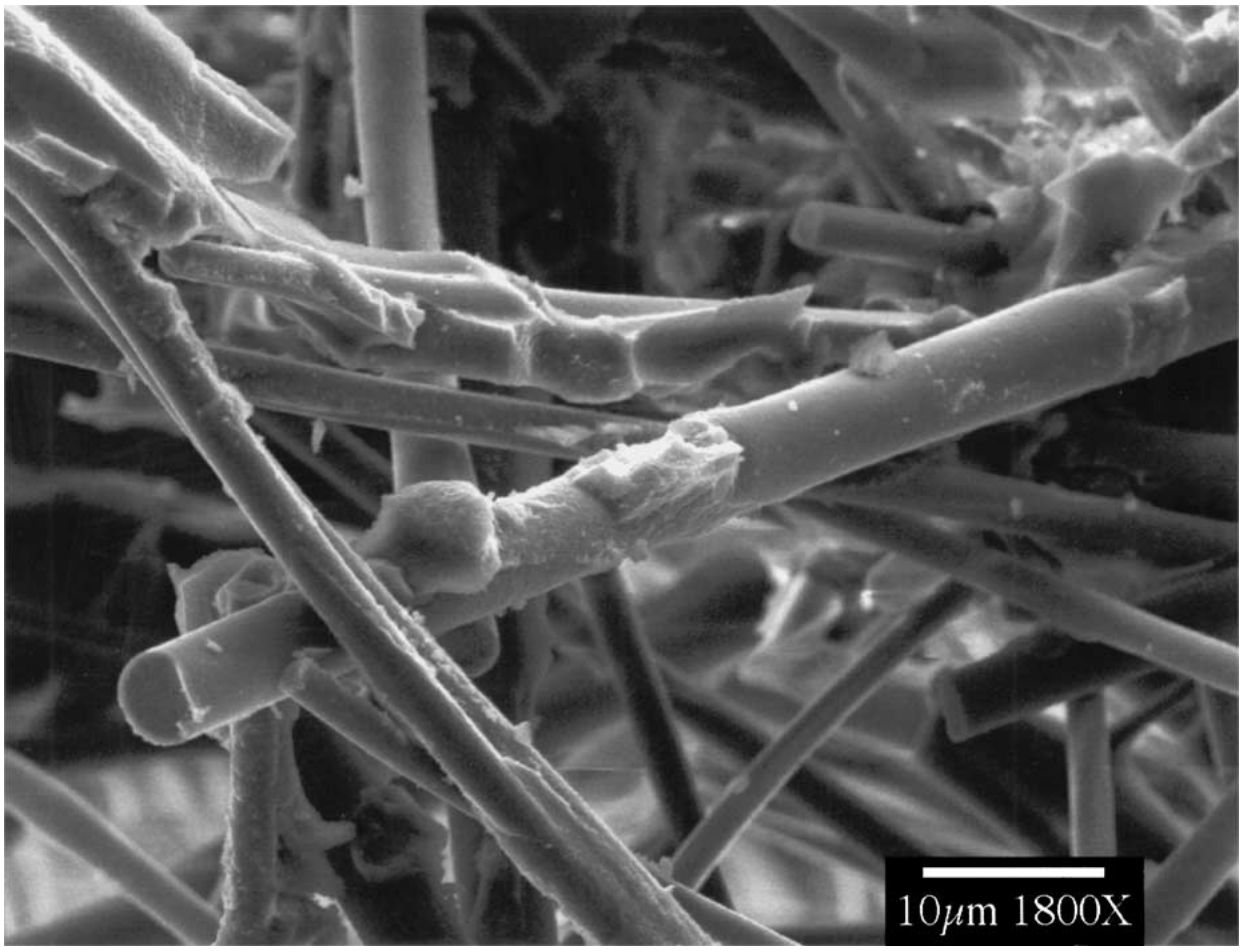

Figure 4 Scanning electron micrograph of a filter membrane with colloidal alumina binder.

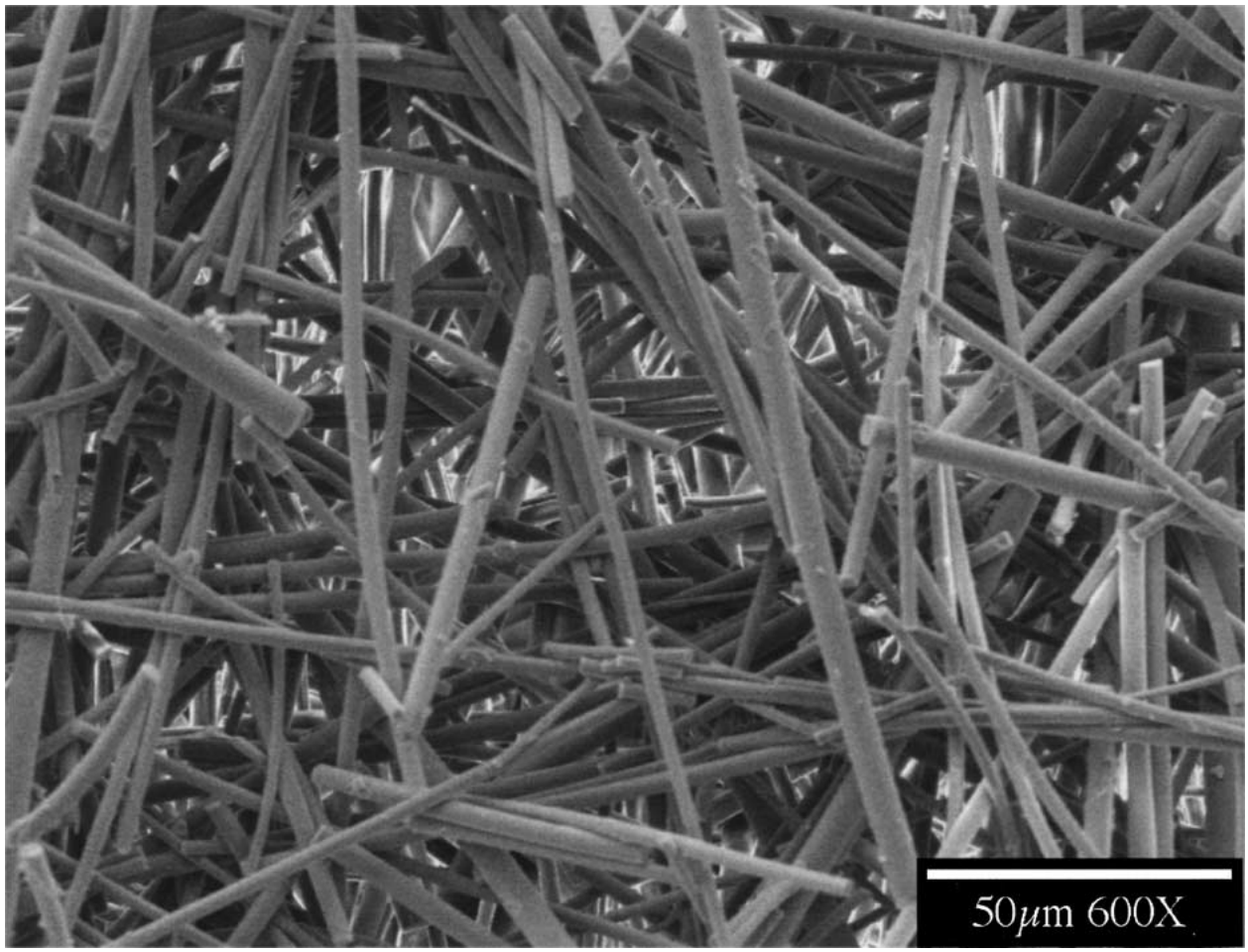

Figure 5 Scanning electron micrograph of a filter membrane with AP23 binder at 9.5 wt% binder content.

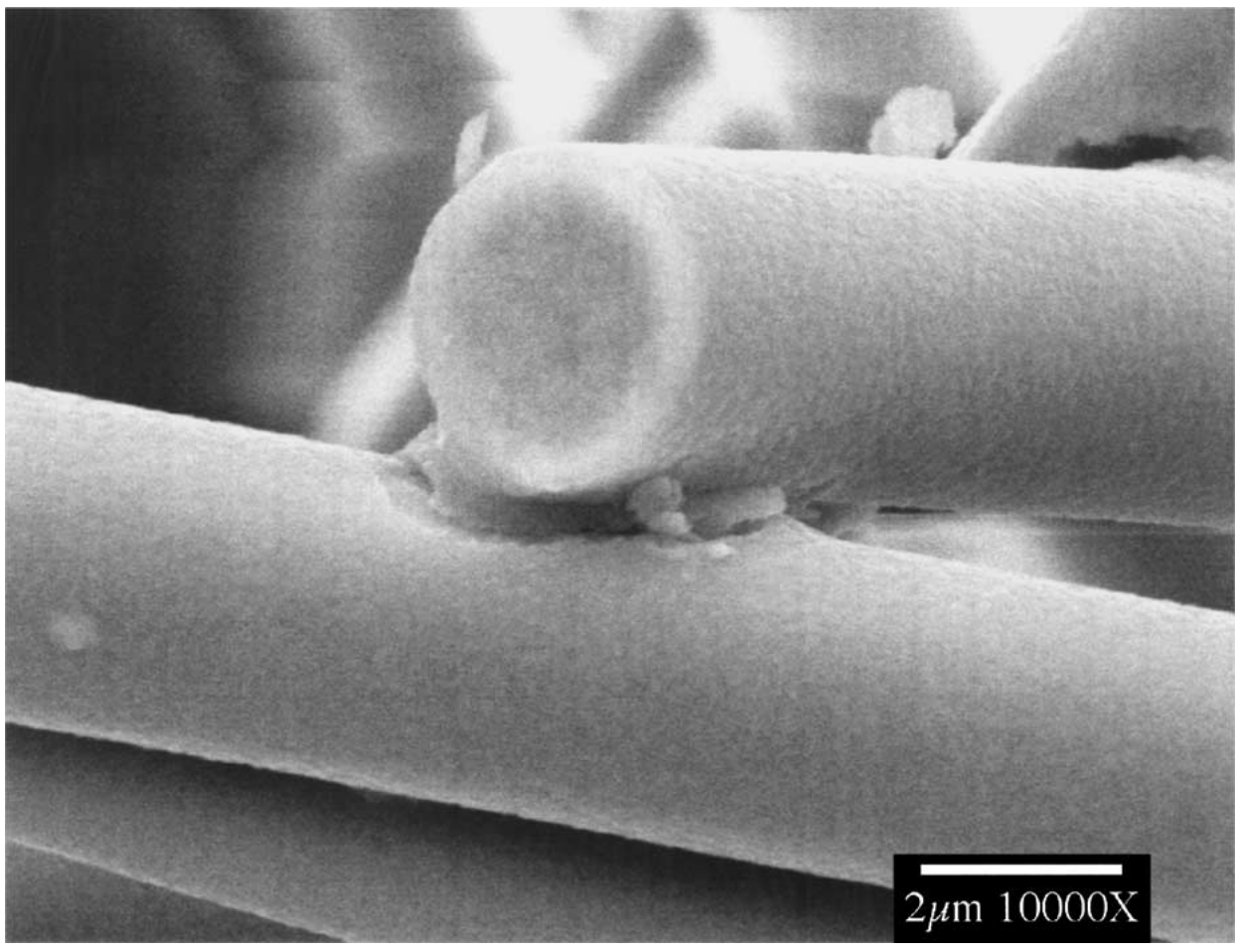

Figure 6 Scanning electron micrograph showing the AP23 binder bonding the junction of two fibers.

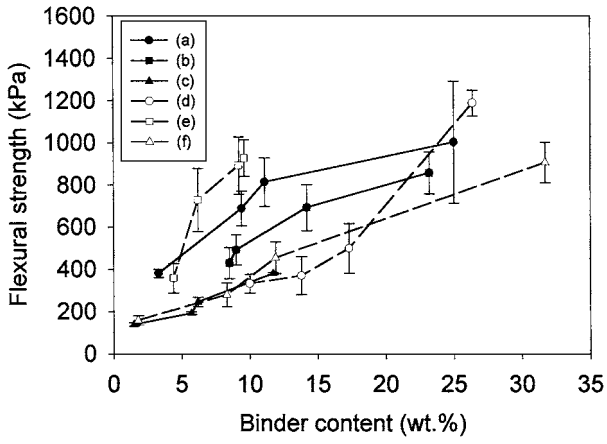

Figure 7 Flexural strength vs. binder amount for various binders: (a) monoaluminum phosphate, (b) colloidal silica (Ludox HS 40), (c) colloidal alumina, (d) colloidal silica (Megasol S50), (e) AP23 binder, (f) colloidal silica (Nalco 2329).

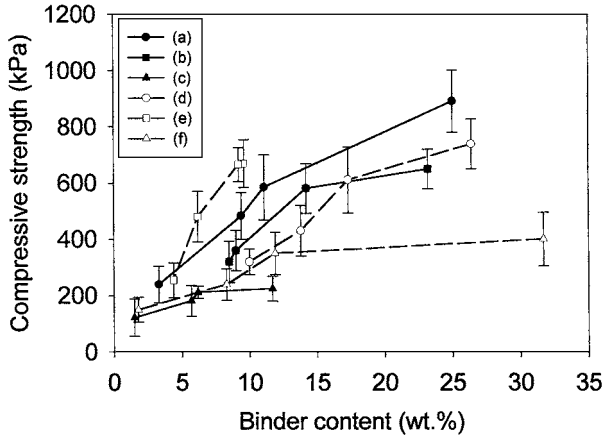

Figure 8 Compressive strength vs. binder amount for various binders: (a) monoaluminum phosphate, (b) colloidal silica (Ludox HS 40), (c) colloidal alumina, (d) colloidal silica (Megasol S50), (e) AP23 binder, (f) colloidal silica (Nalco 2329).

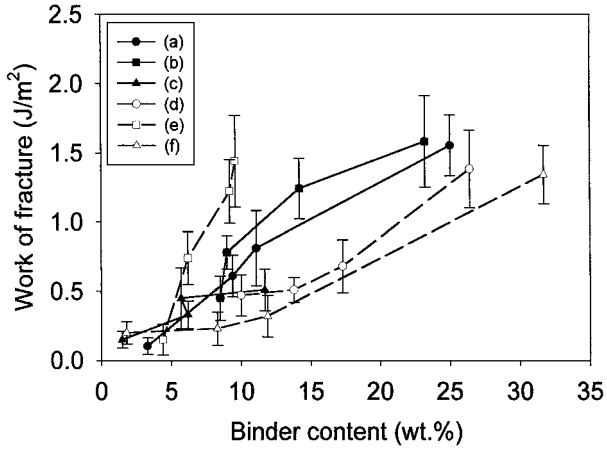

Figure 9 Work of fracture vs. binder amount for various binders: (a) monoaluminum phosphate, (b) colloidal silica (Ludox HS 40), (c) colloidal alumina, (d) colloidal silica (Megasol S50), (e) AP23 binder, (f) colloidal silica (Nalco 2329).

to the response seen for flexural strength (Fig. 9). The AP23 binder samples absorbed more energy during fracture compared to the other binders for binder levels of 5 to 10 wt%. Below 5 wt% it appears that the other binder systems may absorb more energy during fracture. However, the energy required for fracture with

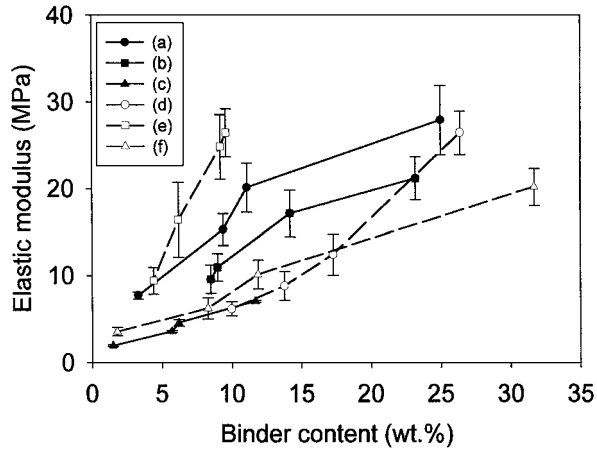

Figure 10 Elastic modulus vs. binder amount for various binders: (a) monoaluminum phosphate, (b) colloidal silica (Ludox HS 40), (c) colloidal alumina, (d) colloidal silica (Megasol S50), (e) AP23 binder, (f) colloidal silica (Nalco 2329).

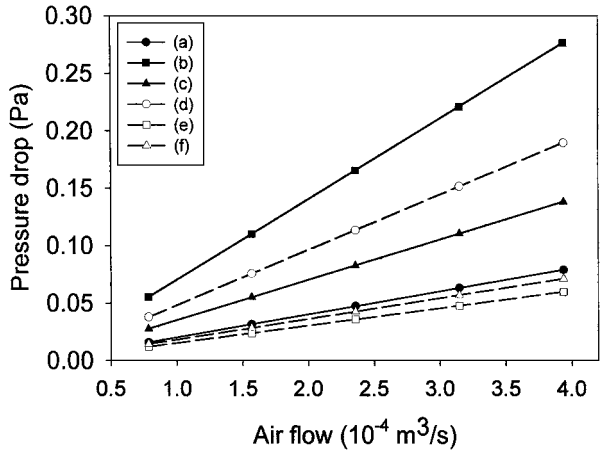

Figure 11 Pressure drop vs. air flow for various binders: (a) 25 wt% monoaluminum phosphate, (b) 23.2 wt% colloidal silica (Ludox HS 40), (c) 11.8 wt% colloidal alumina, (d) 26.4 wt% colloidal silica (Megasol S50), (e) 9.6 wt% AP23 binder, (f) 31.7 wt% colloidal silica (Nalco 2329).

binder levels of less than 5% is relatively small for all binder types.

The Young's modulus, E, was calculated using Equation 2. Fig. 10 shows that significant improvement in the modulus of elasticity can be achieved with AP23 binder contents of 5 to 10 wt%. Similar performance is possible with other binder systems, but only with much higher levels of binder content.

3.3. Pressure drop

Fig. 11 shows the pressure drop vs. air flow through the filter membranes with the different binder systems. Since strength is of primary importance, Fig. 11 compares the pressure drop of samples having approximately the same strength. This is achieved by comparing the samples with different levels of binder that resulted in approximately the same flexural strength. The HS40 colloidal silica appears to have the highest pressure drop in this test. This is most likely due to the small colloid size and its tendency to block the otherwise open fiber structure. Megasol also resulted

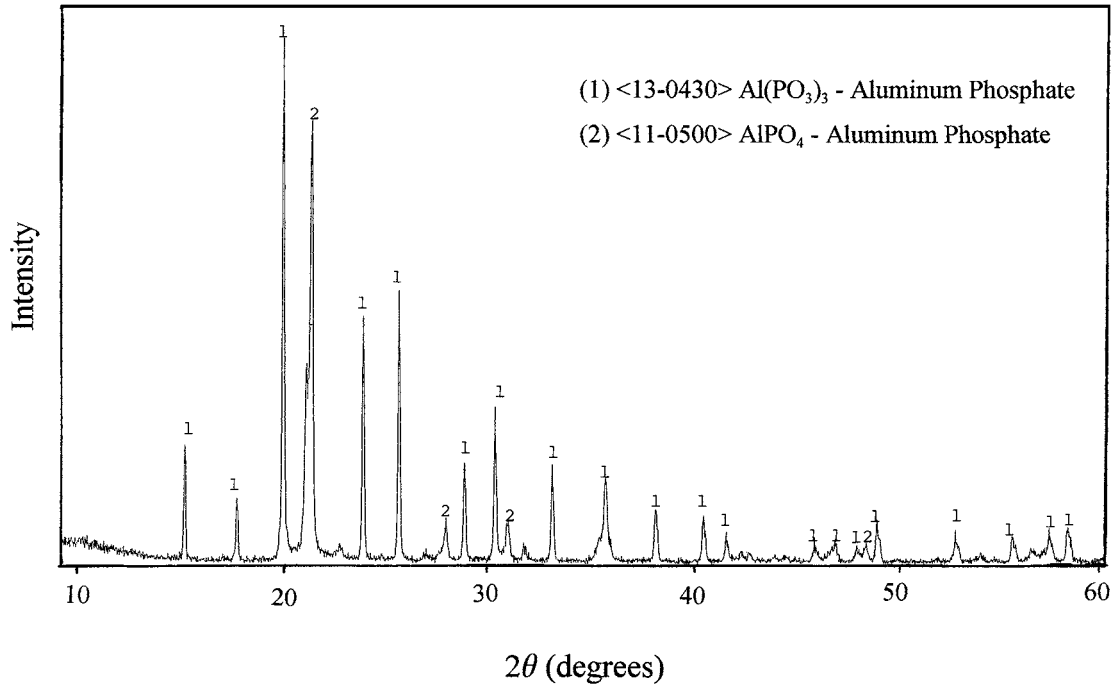

Figure 12 X-ray diffraction pattern of the alumina fiber filter membrane material with AP23 binder at 9.5 wt% binder content.

in a relatively high pressure drop. This again is most likely due to the wide distribution in colloid particle size and its ability to block the open fiber structure. The monoaluminum phosphate, Nalco 2329 and AP23 binders demonstrated relatively low pressure drop, with the AP23 binder sample being marginally better.

3.4. X-ray diffraction

Fig. 12 shows the X-ray diffraction pattern of the filter membranes containing AP23 binder. Results indicate that the 800°C heat treatment for 3 h. resulted in aluminum orthophosphate ($AlPO_4$) and type A aluminum metaphosphate ($Al(PO_3)_3$) being formed as the binder phases. Type A aluminum metaphosphate is a high-temperature phase and is stable to about 1200°C [2]. The cristobalite aluminum orthophosphate has a similar crystal structure to cristobalite silica (SiO_2) such that Al + P in $AlPO_4$ is equivalent to Si_2 in Si_2O_4 [2].

4. Conclusions

This paper compares the mechanical properties and pressure drop characteristics of alumina fiber based filter membranes made using three different types of colloidal silica, colloidal alumina, monoaluminum phosphate and a non-commercial acid phosphate binder. The filter membranes containing between 5% and 10% by weight of acid phosphate binder exhibited the highest flexural strength, compressive strength, work of fracture and elastic modulus in comparison to those containing the other binders at equivalent binder contents. Microscopy showed that the acid phosphate caused the fibers to bond at their junctions only, whereas colloidal alumina and the colloidal silica binders caused free binder particles within the fiber network. The effect of the free binder particles was also seen in the pressure drop results since the free binder particles contributed to the restriction of air flow through the fibrous membrane. The filter membranes containing 9.6 wt% acid phosphate exhibited the lowest pressure drop in comparison to membranes with other binders and having equivalent flexural and compressive strengths.

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