The Technical Suitability & Limitations of PPS Filter Media When Utilized in Utility Boiler Baghouses

Paper # 19

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ABSTRACT

During the last decade, fabric filter baghouses employing pulse jet cleaning systems have trumped those employing reverse air cleaning as the new baghouse of choice by electric utilities. As a result polyphenylene sulfide (PPS) felt bags have been most often employed rather than woven fiberglass bags. At first glance the cost and technical capability of PPS make it an obvious selection, however wide usage has raised questions as to the specific ranges of temperature and chemical exposure capabilities as well as shrinkage.

In the past, PPS was marketed under the Ryton trade name and only produced by Phillips 66 Fibers. Today there are multiple resin suppliers and, in addition, blended fibers are employed. The presence of these variables raises questions as to their impact on PPS filter bag's technical capabilities and life.

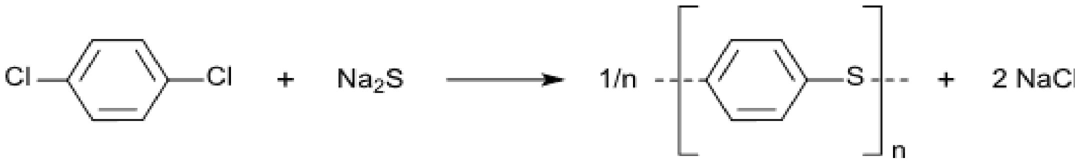
This paper is an attempt to answer a number of these questions by means of laboratory tests including testing of shrinkage, permeability and strength at various temperatures/durations. This work includes the development of temperature versus color charts and Fourier transform infrared spectroscopy (FTIR) analysis of PPS purity. Alternatives to PPS are briefly discussed. Suggestions are made regarding future research and field confirmation required.

INTRODUCTION

Coal-fired boiler (CFB) baghouse applications require a high performance fiber with good thermal and textile properties as well as broad chemical resistance. PPS fibers meet the combination of chemical, thermal, and durability property requirements for CFB fly ash emission capture and do so at a competitive cost.

In 1966 the first U.S. patent was issued to Phillips Petroleum.[1] PPS fiber possesses inherent flame resistance, has exceptional resistance to most chemicals, and has exceptional long-term thermal stability. It has proved to be an outstanding fiber for industrial flue gas filtration applications as a result of its durability and its combination of good thermal and chemical stabilities. PPS resin commercial production was initiated by Phillips Petroleum Company in 1973. In this process, paradichlorobenzene and sodium sulfide are allowed to react in a polar solvent at elevated temperatures, and a linear, *p*-linked aromatic sulfide polymer is formed, shown in Equation 1.[2]

Equation 1. Polyphenylene sulfide preparation



PARADICHLORO-BENZENE **SODIUM SULFLIDE** **POLYPHENYLENE SULFIDE** **SODIUM CHLORIDE**

PPS polymers and mineral- and glass-filled compounds were introduced commercially by Phillips Petroleum Company under the trade name Ryton (registered trademark of Phillips Petroleum Company). Ryton properties include good dimensional stability, inherent flame retardancy, and thermal stability.

As polymerized, the polymer is a light tan, free-flowing powder. It is not soluble in any known solvent below 200°C; above this temperature it has limited solubility in some solvents such as aromatics, chloroaromatics, and heterocyclic compounds. PPS can exist in either the amorphous or the crystalline state. PPS staple fiber became available in commercial quantities in early 1983.

In 1986 the Federal Trade Commission (FTC) found PPS to be outside the current classes and thereby granted a new generic named Sulfar.[3] Sulfar is "a long chain synthetic polysulfide with at least 85% of the sulfide linkages attached directly to two aromatic rings." Early on it was touted as suitable for filter bags for filtration of flue gas from CFBs. Based on long term (8000 hrs) exposure time testing, the maximum recommended operating temperatures were found to be 375°F (190°C) continuously and 450°F (232°C) for short term surges. Resistance to acids and alkalis was found to be "outstanding."[3] In addition PPS was classified as nonflammable. More recent study of CFB field installations have proven life of 5 plus years.

Shrinkage of PPS in the early years was relatively high. In 1978 it was reported to be 28% (130°C), but by 1988 "normal" shrinkage was 4%.[4] Today it can be controlled to 1% or less. At a 1988 Ryton Filtration Seminar[4], in addition to the positive comments on the product, it was also noted that it dissolved in bromine gas and there were concerns regarding oxygen concentrations above 9% in combination with normal CFB gas temperatures (375°F).[5] At that time most felts were supported with a "scrim" of woven yarns and a polytetrafluoroethylene (PTFE) scrim was recommended. Later PPS scrim was found suitable and in the last two decades scrimless (fiber supported) felts have been proven durable. Successful Ryton bags in Europe were noted along with two U.S. CFB pulse jet applications. In 1991 Phillips published a number of case histories of trouble-free 24 month plus service life for coal fired boilers, waste-to-energy (WtE) facilities and biomass CFB units. Maximum bag life of 36 months minimum was touted since Ryton "does not hydrolyze, moisture is not a concern."[6] A separate Phillips document noted that outlet emissions are below 0.005 pounds per million Btu (lbs/mmBtu) for Ryton felt.[7] A 2003 Chevron Phillips technical service memo distinguishes between high molecular weight (HMW) linear PPS and HMW branched PPS. Therein it is noted that the higher tenacity, elongation, and impact strength make the linear PPS ideal for fibers, whereas the branched is suitable for films.[8] By 2010 McIlvaine reported that CP Chem (Chevron Phillips), Toray and Ticona (Celanese) offer

PPS resin and Inspec, Amoco Fiber and Toray make the fibers. In the U. S., Southern Felt Company provides PPS felt to many of the domestic bag manufacturers. McIlvaine also notes that "branched PPS, the older of the two forms, is rigid and generally not suitable for extrusion."[9]

Because of its temperature and acid resistance capability PPS felt, at this point in time, has captured the vast majority of utility CFB pulse-jet baghouses. A few units have opted for P84 (polyimide) felt. Five year life for PPS felt bags has been demonstrated on coal-fired utility boilers. In a few cases ePTFE membrane has been utilized in conjunction with PPS felt for improved filtration of fine particles 2.5µm and under. Approximately 280 baghouses have been installed on utility CFB baghouses in the United States. About half of the CFB utility baghouses are pulse-jets with PPS and the other half are reverse-air with woven fiberglass. The older units are generally reverse-air.[10]

SPECIFICATIONS AND TEST METHODS

Specifications

PPS felt fabric used for manufacturing filter bags in electric utility baghouse applications is generally specified as 100% PPS fibers with or without an ePTFE membrane; however, blends of PPS and P84 fibers have been utilized as well. For applications with 100% PPS felt, some of the typical specification values are listed with the description of each laboratory test below.

Air Permeability

The air permeability test is used to determine the amount of air that can flow through a given cloth area. Permeability is defined in ASTM Standard D737 as the rate of air flow passing perpendicularly through a known area of fabric which is adjusted to obtain a prescribed air pressure differential between the two fabric surfaces.[11] From this rate of air flow, the air permeability of the fabric can be determined in units of $ft^3/ft^2/min$ (ft/min). For the testing performed in this study, a Frazier Differential Air Permeability Measuring Instrument was used at 0.5 inches of water pressure differential. The permeability of clean PPS felts used in fabric filter bags (15-17 oz/yd^2) typically ranges between 20-45 ft/min, while clean PPS felts laminated with ePTFE membrane typically range from 3-12 ft/min.

Fabric Thermal Stability (% Shrinkage)

The fabric thermal stability (% shrinkage) is used to measure how much the fabric changes dimensionally when exposed to specific temperatures. The warp (machine direction) and fill (cross machine direction) dimensions of a fabric swatch were measured to the nearest 0.5 millimeter (mm). The test samples were then suspended unsupported in an oven, set at varying temperatures of 300°F, 400°F, and 500°F (typically 400°F for standard laboratory testing), for various time durations (typically 2 hours for standard laboratory testing). The samples were then removed from the oven, allowed to cool, and their dimensions were then re-measured at the same fabric locations. PPS felt is typically specified with a maximum shrinkage of 2% at 400°F for 2 hours, however, that characteristic can be controlled to lower values with heat setting and has been specified to less than 1% in certain applications.

Mullen Burst

The Mullen burst strength test, described in ASTM Standard D3786, is designed to show the relative total strength of fabrics to withstand severe pulsing or pressure. Fabric strength is measured by determining the difference between the total pressure required to rupture the specimen and the pressure required to inflate an expandable diaphragm in units of pounds per square inch (lbs/in^2 or psi).[12] PPS felt weighing 15-17 oz/yd^2 is typically specified with a minimum Mullen burst of 380-450 psi.

Tensile Strength

The tensile strength test provides data on fabric strength and elongation. The ASTM Standard D5035 provides raveled strip (woven fabrics) and cut strip test procedures (nonwoven and felted fabrics) for determining the breaking force and elongation of most textile fabrics.[13] The fabric samples utilized in this study were all cut to 1 inch in width by 6 inches in length. The samples were then clamped in the jaws of the tensile test apparatus with a distance between the clamps set at 3 inches. The test apparatus was started, causing the jaws to move apart and the fabric to stretch until breakage. The tensile strengths, expressed in units of pounds-force per inch (lb/inch), were recorded for fabric prepared in both the warp and fill directions, however, the fabric elongation was not measured. Commercial product specifications are not always available for tensile strength and if so, the units may also be expressed as lb/2 inch wide strip. ETS technical specifications for PPS felt weighing15-17oz/yd^2 often call for 85-100 lb/inch minimum in the warp direction and 95-100 lb/inch minimum in the fill direction.

M.I.T. Flex Endurance Test

The M.I.T. flex endurance test primarily measures the relative value of fabric to withstand self-abrasion from flexing by measuring the number of flex cycles necessary to break a fabric sample. The test method is described in ASTM Standard D2176, which is the standard method for testing the folding endurance of paper.[14] The fabric samples are tested in both the warp and fill directions.

A swatch of fabric exactly 0.5 inches in width and approximately 5 inches long is cut and clamped firmly into the machine jaws. The fabric is folded/flexed as a spring and cam mechanism moves back and forth through an angle of 135°. The number of folds is recorded until the fabric breaks. The M.I.T. test machine uses a 4 lb dead weight load and a #8 spring. The spring acts as a shock absorber to ensure uniformity of load.

The M.I.T. flex test has traditionally been used to help determine the rate of deterioration of woven fiberglass bags used in coal-fired utility boilers due to the inherent abrasiveness of glass fibers. ETS, Inc. has also found the M.I.T. flex test to be very useful in the evaluation of PPS felt and its ability to withstand flexing against a wire cage during pulse cleaning cycles. For nearly all filter bag fabric types, this test can be a leading indicator that the fabric is nearing the end of its useful service life. Commercial product specifications are not generally available for M.I.T. flex endurance. ETS technical specifications often call for 10,000 flexes minimum in both the warp and fill directions for PPS felt.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a technique that uses infrared light to observe properties of a solid, liquid, or gas. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. FTIR analysis results are generally utilized for identification of materials of construction (e.g., fiber type, thread type) of filter bags and /or evaluation of contaminants.

Comprehensive Testing

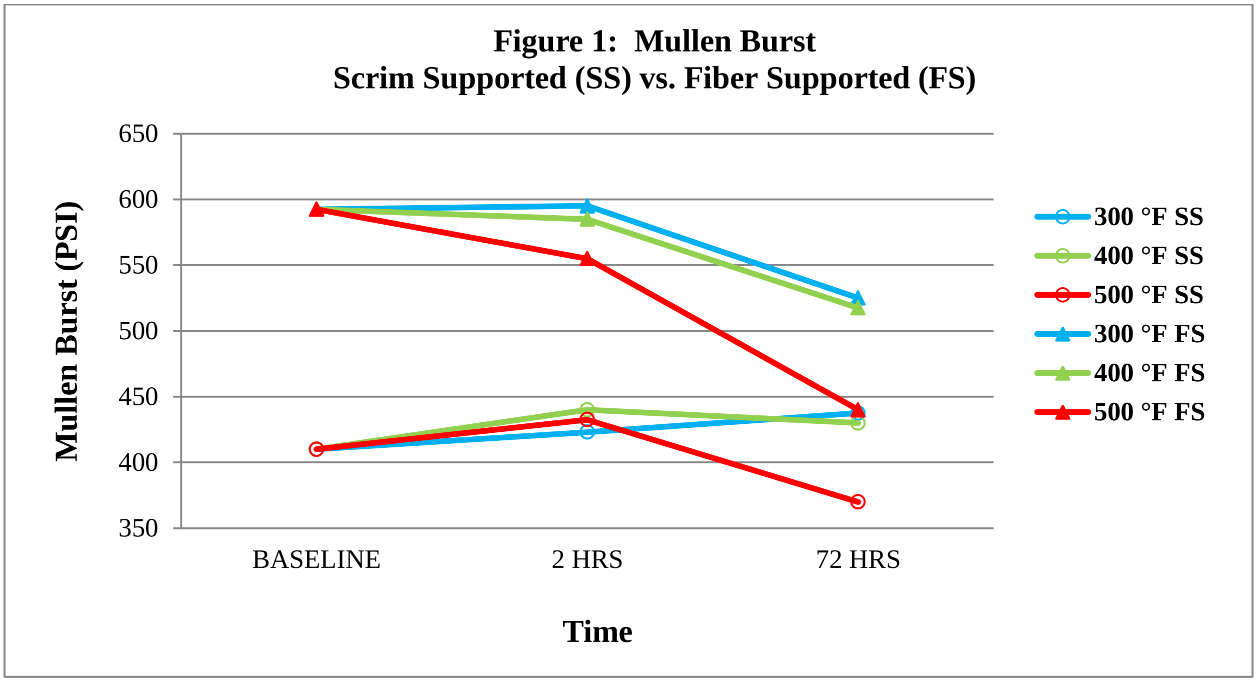
All of the strength and flow tests should be done in conjunction with each other periodically in order to develop the loss of strength and flow trend lines over time. Often the M.I.T. flex test will be the leading indicator of potential failure. The testing program can identify when the bags are approaching end of life and higher risk of failure, but cannot predict the exact timing of end of life of the bag set. Permeability measurements of used bags can, by varying the amount of vacuuming, help to determine if the bags are gradually blinding (losing permeability). Used bag test values are compared with original clean fabric test values to show rate and level of deterioration.

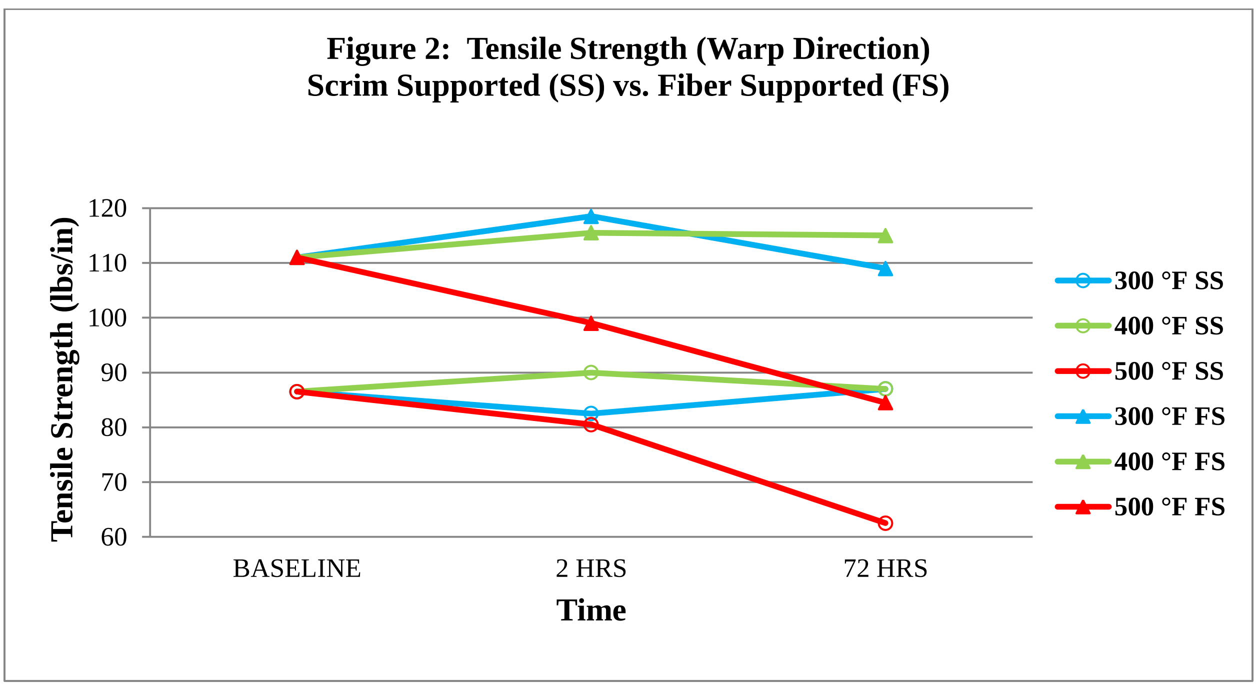
EXPERIMENTAL DATA

PPS Time and Temperature Study

A time and temperature study was conducted on two domestically manufactured, 16 oz/yd^2, plain finish, PPS fabric samples of reportedly similar specification, with the primary difference being the manufacturing method of the finished felt. Sample A was constructed as a scrim supported needlefelt, while sample B was constructed as a fiber supported (scrimless) needlefelt. The fabrics were tested for weight, air permeability, fabric thermal stability (% shrinkage), Mullen burst, tensile strength and M.I.T. flex endurance at three different temperatures (300°F, 400°F, and 500°F) and time intervals (baseline, after 2 hours, and after 72 hours).

In comparing the strength properties of the scrim supported versus the fiber supported PPS, the fiber supported had higher Mullen burst and tensile strength values in both the warp and fill directions than did the scrim supported at the same temperatures and times (Figures 1, 2, and 3). The individual values of both the fiber supported and scrim supported felts, however, were all still above the typical specification minimums for PPS felt with the exception of the values at 500°F for 72 hours, which indicated a significant decline in strength (25.8% of the baseline value for fiber supported and 9.8% of the baseline value for scrim supported). The fabric shrinkage was considerably lower in both the warp and fill directions for the fiber supported PPS in comparison to the scrim supported PPS (Figures 4 and 5), but the values were fairly typical for both fabric types at the 300°F and 400°F temperatures. After exposure to 500°F for only 2 hours, the % shrinkage for the fiber supported PPS was 4.4% in the warp direction and 3.5% in the fill direction, while the scrim supported was twice as much in the warp direction at 8.8% and 5.2% in the fill direction. In contrast, the M.I.T. flex endurance values in both the warp and fill directions were significantly higher for the scrim supported in comparison to the fiber supported. Like most of the other laboratory tests, the M.I.T. flex endurance values also showed a notable decline after 72 hours of exposure to 500°F (Figures 6 and 7). The air permeability values did not differ dramatically between the scrim supported and fiber supported felts and only decreased slightly after exposure to 500°F (Figure 8).





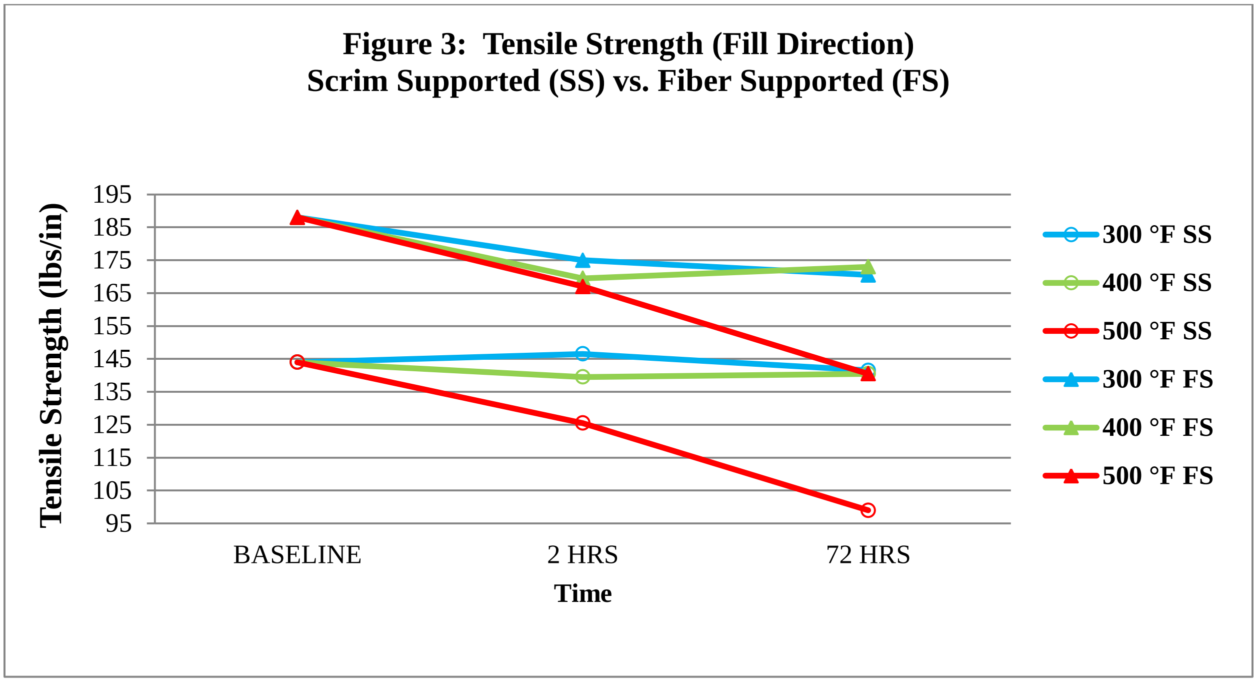


Figure 3: Tensile Strength (Fill Direction)
Scrim Supported (SS) vs. Fiber Supported (FS)
Tensile Strength (lbs/in)
195
185
175
165
155
145
135
125
115
105
95
BASELINE
2 HRS
72 HRS
Time
300 °F SS
400 °F SS
500 °F SS
300 °F FS
400 °F FS
500 °F FS

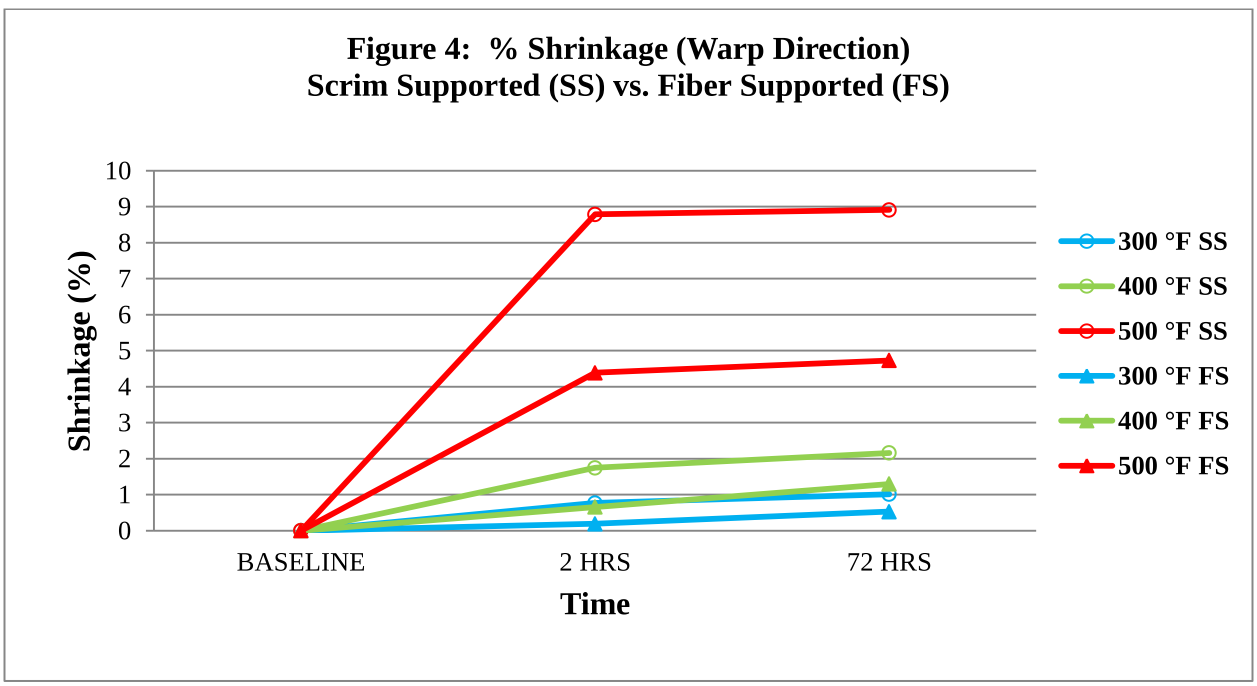


Figure 4: % Shrinkage (Warp Direction)
Scrim Supported (SS) vs. Fiber Supported (FS)
Shrinkage (%)
10
9
8
7
6
5
4
3
2
1
0
BASELINE
2 HRS
72 HRS
Time
300 °F SS
400 °F SS
500 °F SS
300 °F FS
400 °F FS
500 °F FS

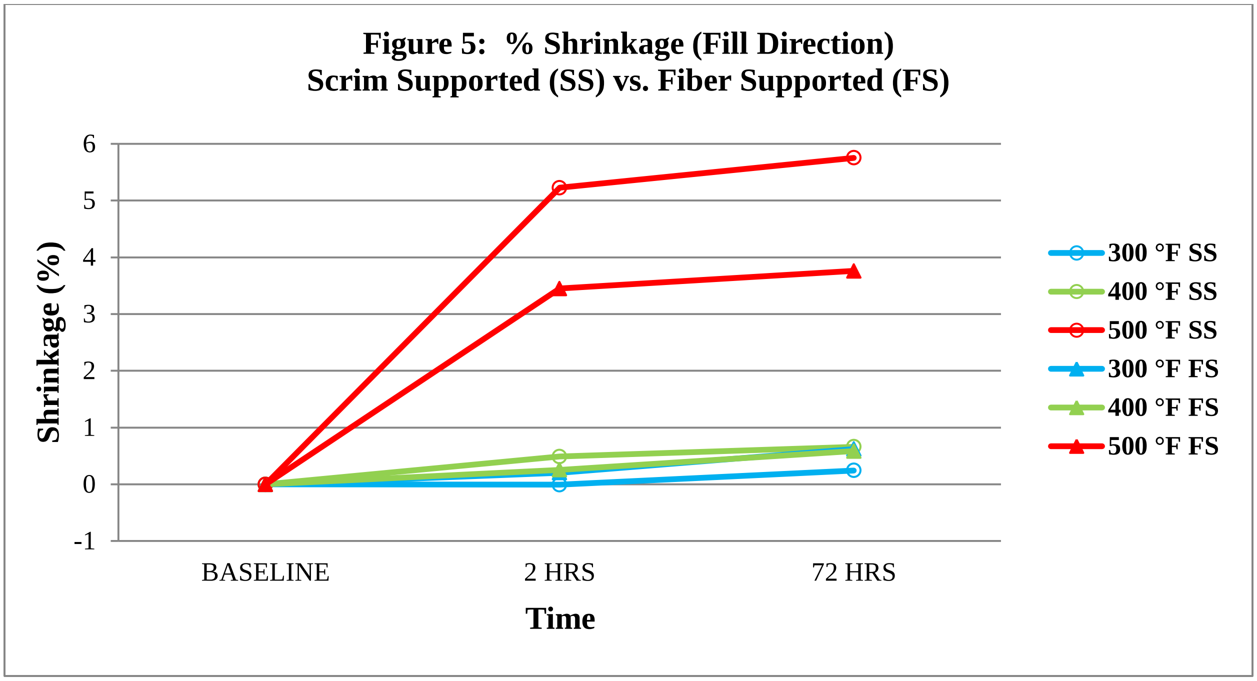


Figure 5: % Shrinkage (Fill Direction)
Scrim Supported (SS) vs. Fiber Supported (FS)
Shrinkage (%)
6
5
4
3
2
1
0
-1
BASELINE
2 HRS
72 HRS
Time
300 °F SS
400 °F SS
500 °F SS
300 °F FS
400 °F FS
500 °F FS

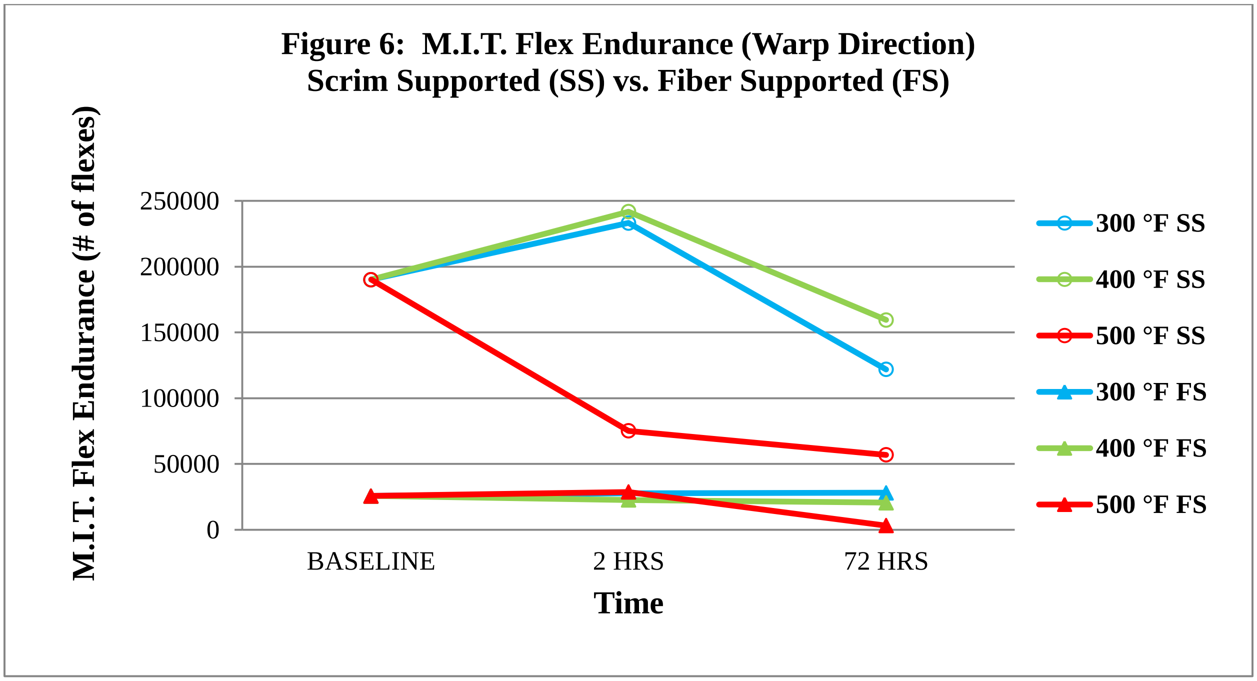
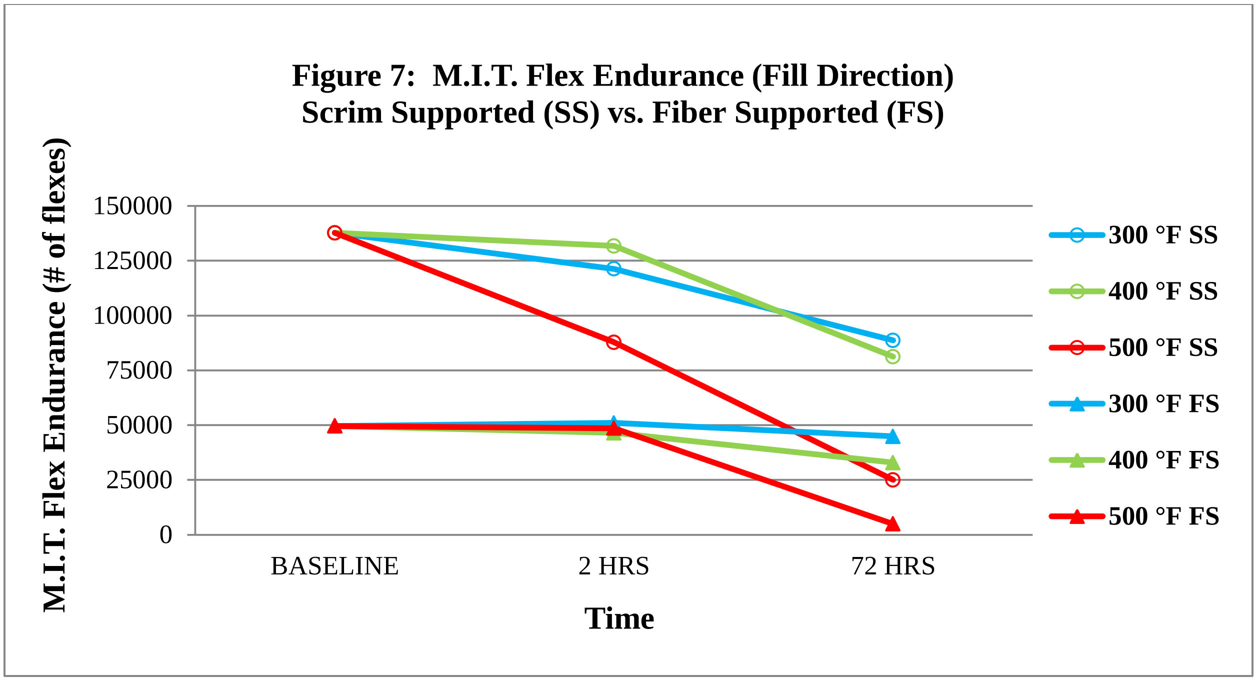
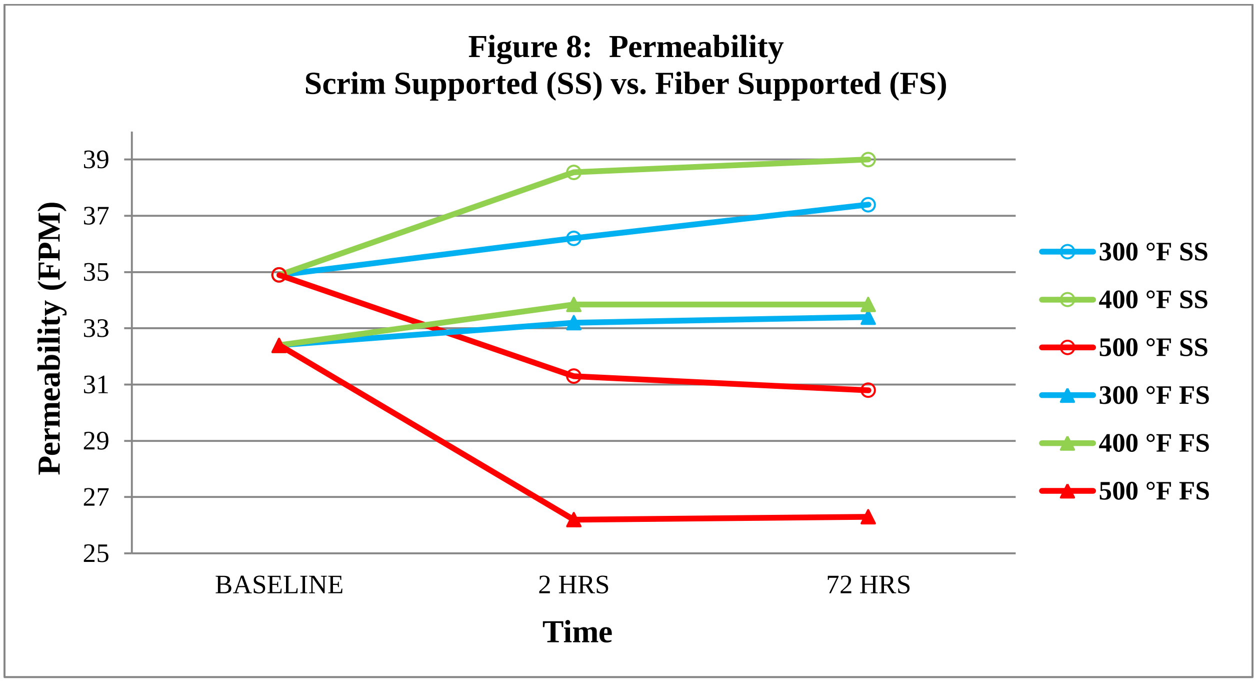


Figure 6: M.I.T. Flex Endurance (Warp Direction)
Scrim Supported (SS) vs. Fiber Supported (FS)
M.I.T. Flex Endurance (# of flexes)
250000
200000
150000
100000
50000
0
BASELINE
2 HRS
72 HRS
Time
300 °F SS
400 °F SS
500 °F SS
300 °F FS
400 °F FS
500 °F FS





In addition to the laboratory testing conducted on fabric samples A and B above, the same tests were conducted on three imported PPS felts at baseline conditions and after 2 hours at 400°F. Fabric sample C was reported to be a 16 oz/yd^2 fiber supported PPS felt with one side singed, sample D was reported to be a 15 oz/yd^2 scrim supported PPS felt with an ePTFE membrane, and sample E was reported to be a 17 oz/yd^2 scrim supported PPS felt with one side singed. The specific fabric characteristics of samples A through E and all baseline data may be found in Table 1. The results of testing after 2 hours at 400°F for samples A through E may be found in Table 2.

Table 1. Summary of PPS Fabric Characteristics and Baseline Testing Data

Fabric ID		**A**	**B**	**C**	**D**	**E**
Scrim/Fiber Supported		Scrim	Fiber	Fiber	Scrim	Scrim
Fabric Finish		Plain	Plain	Singed	ePTFE membrane	Singed
Spec. Weight, oz/yd^2		16	16	16	15	17
Manufacturing Location		Domestic	Domestic	Imported	Imported	Imported
Tests Performed:						
Weight, oz/yd^2		15.1	16.4	15.4	14.9	18.8
Permeability, fpm		34.9	32.4	38.6	5.9	35.8
Shrinkage, %	Warp	N/A	N/A	N/A	N/A	N/A
	Fill	N/A	N/A	N/A	N/A	N/A
Mullen Burst, psi		410	593	588	520	400
Tensile Strength, lb/inch	Warp	87	111	124	103	97
	Fill	144	188	106	156	96
M.I.T. Flex, # of flexes	Warp	190220	25728	32167	421324	118669
	Fill	137731	49642	44727	129953	70816

Table 2. Summary of PPS Fabric Characteristics and Testing Data After 2 Hours at 400°F

Fabric ID		**A**	**B**	**C**	**D**	**E**
Scrim/Fiber Supported		Scrim	Fiber	Fiber	Scrim	Scrim
Fabric Finish		Plain	Plain	Singed	ePTFE membrane	Singed
Spec. Weight, oz/yd^2		16	16	16	15	17
Manufacturing Location		Domestic	Domestic	Imported	Imported	Imported
Tests Performed:						
Weight, oz/yd^2		14.9	16.2	15.4	14.8	18.8
Permeability, fpm		38.6	33.9	38.8	6.6	37.0
Shrinkage, %	Warp	1.75	0.66	0.68	3.14	3.60
	Fill	0.49	0.25	-0.29	3.76	-0.39
Mullen Burst, psi		440	585	580	530	485
Tensile Strength, lb/inch	Warp	90	116	140	107	107
	Fill	140	170	128	153	112
M.I.T. Flex, # of flexes	Warp	241888	22676	25488	292784	156640
	Fill	131724	46506	32501	73312	74480

The following observations were noted in the data:

- All baseline fabric weights were within ± 1 oz/yd^2 of their specification weight with the exception of sample E
- Permeability of sample D was much lower than other samples due to ePTFE membrane
- Baseline Mullen burst value of sample E was lower than expected at 400 psi for a scrim supported felt weighing 18.8 oz/yd^2

- Mullen burst baseline and after 2 hours at 400°F values were higher for fiber supported PPS in comparison to scrim supported PPS
- M.I.T. flex endurance baseline and after 2 hours at 400°F values were significantly higher for scrim supported PPS in comparison to fiber supported
- % shrinkage values were lower for fiber supported in comparison to scrim supported
- % shrinkage values in the warp direction for imported, scrim supported PPS (samples D and E) were more than 75% higher than domestic scrim supported PPS (sample A)
- % shrinkage value in the fill direction for the imported sample D was considerably higher than all other samples

PPS Color Charts

Figure 9 depicts the effects of temperature at different time durations on the color of PPS felt. The typical color of PPS felt, as shown by the baseline samples, is off-white can be slightly darker if the felt has undergone a finishing process such as singeing. At the 300°F and 400°F conditions, both the scrim supported and fiber supported fabrics remained relatively unchanged in color, with a slight color change to light tan after the extended time (72 hours) at 400°F. The more noticeable color change occurred after only 2 hours at 500°F in which both fabric samples turned tan in color. After 72 hours at 500°F, the samples were significantly darker with a medium brown color. Based on this laboratory study, exceeding the recommended continuous operating temperature of 375°F of typical PPS felts will have a noticeable color change on the fabric and can be a useful tool in troubleshooting premature bag failures. It should be noted that during typical baghouse operations, other factors such as the particulate being filtered and the chemical constituents of the dirty gas stream may also affect the resulting color of the PPS felt fabric.

Figure 9: Color Changes Throughout Time vs. Temperature Study of Scrim Supported and Fiber Supported PPS Felt

PPS FTIR Analysis

In addition to the five samples previously mentioned (A through E), two additional domestically manufactured PPS felts (F and G) were evaluated by FTIR. Sample F was reported to be a 16 oz/yd^2 scrim supported PPS felt with one side singed and sample G was reported to be a 16 oz/yd^2 scrim supported PPS felt with an ePTFE membrane on one side. Initially, the IR Spectra of both sides of all seven PPS fabric samples (A through G) were evaluated to confirm that the composition corresponded to known IR Spectra of 100% PPS felt. All seven samples indicated normal PPS fabric; however, sample E had a trace of polyester absorbance on one side. Both samples D and G indicated polytetrafluoroethylene (PTFE) coating over the PPS on one side consistent with specifications for the collection sides to have an ePTFE membrane. Sample D also indicated a lighter PTFE coating on the non-collection side which is atypical for filter bags.

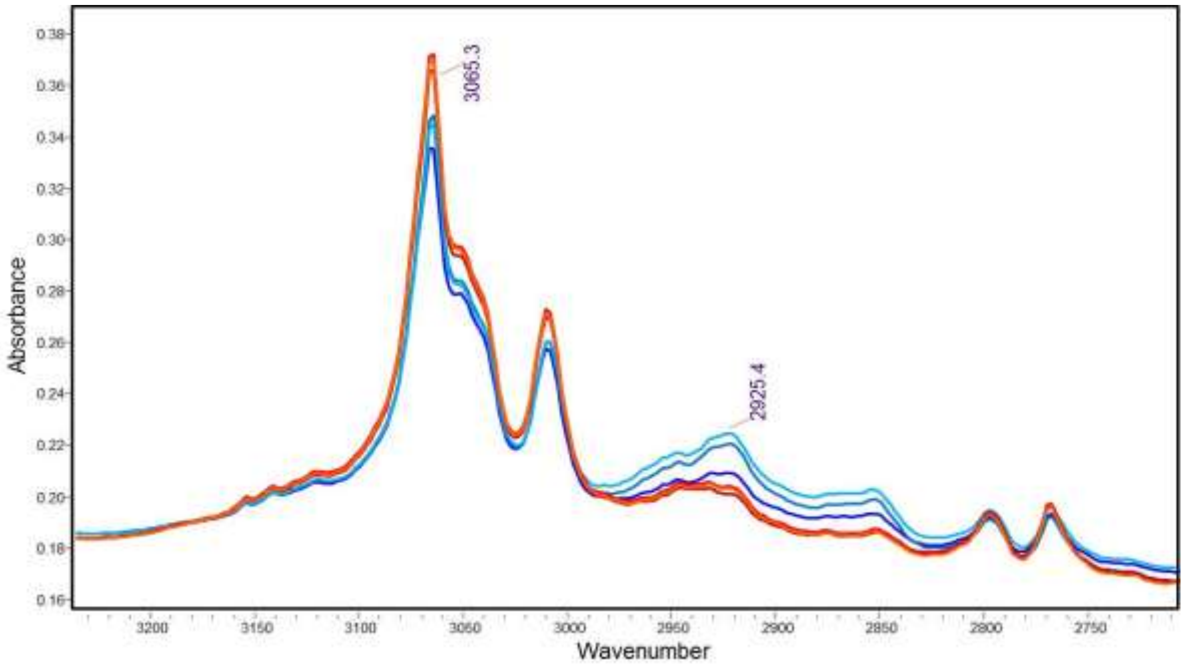
Additional FTIR analysis was performed on samples D and G using a more sensitive hot pressing technique to see if differences could be detected in PPS fibers removed from the two fabrics. The overlaid FTIR spectra of both sample D and sample G after preparation as hot pressed thin films indicated additional PTFE in sample D (1257cm^{-1} and 1153cm^{-1}), as well as very weak bands for additional polyester (polyterephthalate, PET, 1730cm^{-1}). Sample D also indicated very weak additional aliphatic hydrocarbons (2925cm^{-1}), possibly polyethylene, additive or oil residue.[15]

In order to determine variations in the PPS fibers such as manufacturing from linear or branched resin, peak area ratios for only PPS related absorbance bands were defined and compared to all three replicates of each sample. The reference aromatic ring quadrant stretch peak at 1574cm^{-1} should be similar in both branched and linear PPS. The aromatic CH stretch (3065cm^{-1}) is dependent on the degree of substitutions on the aromatic ring. Therefore, purely linear PPS would produce only para aromatic ring substitution (4 CH stretch groups per aromatic ring), and branched would have para with additional 1,3,4 or 1,3,4,5 aromatic substitutions. This would effectively lower the total aromatic CH stretch ratio to aromatic ring stretch. This absorbance ratio is observed as shown in Table 3, in which sample D indicates less aromatic CH ratio and thus more branched substitution. The difference is not large but is consistent for all the replicates (Figure 10). This most likely indicates only a small percentage of the PPS is branched in sample D.[15]

Table 3. The IR Peak Area Ratios for Aromatic CH Stretch (3065cm^{-1}/1573cm^{-1}) and Aliphatic CH Stretch (2925cm^{-1}/1573cm^{-1})

Sample Name	Aromatic CH	Aliphatics
25µm pps film sample G R3	0.966	0.339
25µm pps film sample G R2	0.925	0.311
25µm pps film sample G R1	0.954	0.335
25µm pps film sample D R3	0.841	0.382
25µm pps film sample D R2	0.861	0.511
25µm pps film sample D R1	0.890	0.552

Figure 10: **The Overlaid FTIR Spectra of All Sample D (Blues) and Sample G (Reds) Replicates**



RECOMMENDATIONS

While this paper reports on a fair amount of PPS laboratory testing, it raises as many questions as it answers. The program at this stage does not include studies on the impact of chemical exposure. In addition, the FTIR studies need to be expanded with regards to branched versus linear PPS resins. As the emission codes become more and more stringent, PPS felt detailed specification and quality assurance/quality control verification increase in importance as does preventive and rapid response maintenance. Field case studies of premature bag failure need to include rigorous definition of the inlet gas constituents as well as temperature extremes and duration. Such information will assist in defining the limitations and capabilities of not only PPS and P84, but also any new candidate felts. Emission data will now need to include $PM_{2.5}$ measurements so that comparison with lab filtration performance results can be made.

The importance of FTIR testing to determine branched versus linear PPS resin cannot be overstated, especially when it comes to bag life and bag life guarantees. While there is little field data available for verification of the lab studies indicating the shortcomings of branched PPS for filter bag applications, the lab results are consistent enough to put the suppliers and end users on notice of expected shortened bag life if branched PPS is employed.

Finally it is noted that with many new producers entering the market, a wide variation in test results has been experienced, thus the importance of laboratory round robins and increasing the amount of public data will help to reduce the potential damage of poorer quality PPS felt entering the market.

ACKNOWLEDGEMENTS

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KEYWORDS

Baghouse, Particulate Emissions, Polyphenylene Sulfide (PPS) Felt, Coal-Fired Boilers