OXIDATIVE RESISTANCE OF SULFONE POLYMERS TO CHLORINATED POTABLE WATER

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Abstract

Environmental factors are known to significantly impact the oxidative failure mechanism of plastics. The chlorine present in potable water as a disinfectant is an oxidant and has been shown to be able to significantly affect the failure mechanism of materials in potable water applications. In this paper, the impact of chlorinated potable water on four polysulfone materials was examined (PSU, PPSU/PSU blend, PPSU and glass-reinforced PSU). The materials were tested in the form of standard commercial insert fittings for plastic piping applications and exposed to continuously flowing aggressive chlorinated potable water at elevated temperature and pressure. The exposure period was chosen as twice the lifetime of the adjoining cross-linked polyethylene pipe (PEX) at the test condition. The exposure is shown not to have impacted the mechanical strength of the fittings when compared to the application pipe. Degradation, attributed to oxidation, of the exposed surface was observed. The morphological and chemical changes were examined using SEM, EDX and EDS. The differences between materials are presented. All materials were found to have excellent oxidative resistance to the chlorinated potable water at the tested condition. The PPSU material is seen to be the most resistant while the PSU materials the least resistant. The PPSU/PSU blend resistance was seen to be between that of the PPSU and PSU materials.

Background

Plastic piping and the associated fittings are commonly used in the transportation and distribution of potable water to industrial, commercial and residential facilities. Environmental factors, and their effect on piping materials, such as installation methods and operating conditions have been well characterized[1]. The influence of the transported fluid on piping materials is becoming better understood, particularly for PEX tubing[2,3].

The chlorine residual employed to disinfect potable water is known to increase the oxidative potential of the water in question. The effect of the chlorine residual on PEX pipe has been shown to be primarily an oxidative one[4]. Estimated pipe test lifetimes have been directly correlated to the level of oxidative strength of the potable water. No such analysis has been made to assess the performance of fitting materials in this environment.

In this work, the impact of chlorinated potable water on four polysulfone materials was examined (PPSU, PSU, a PPSU/PSU blend and a glass-reinforced PSU). It is shown that the materials were found to have excellent oxidative resistance to the chlorinated potable water at the test condition.

Experimental

Testing was performed in three phases. The first phase involved exposing specimens to chlorinated water at 115ºC (239°F) for approximately twice the test lifetime, at the same condition, of a commercial ASTM F876 ½” SDR 9 PEX[5] pipe material listed by NSF International to the NSF P171 Protocol[6] for hot water Continuous Re-circulation applications. Testing was performed in general accordance with the ASTM F2023[7] test method at a single test temperature and pressure. The second phase consisted of burst testing the exposed fitting specimens at 93.3ºC (200ºF) in accordance with ASTM D1599-99[8]. Finally, the third phase included subjecting the exposed specimens to the Excessive Temperature and Pressure Test (Sustained 1 MPa (150 psig) pressure at 99ºC (210ºF) for 48 hours) in accordance with CSA B137.5-99 Section 4.9[9].

Four different materials were evaluated in the form of injection molded ASTM standard insert fittings used for PEX piping. The materials tested were polyphenylsulfone (Radel® R-5100, PPSU), polysulfone (UDEL® P-1700, PSU), a blend of PPSU and PSU (ACUDEL® 22000) and a glass fibre re-inforced PSU (UDEL® GF-120), all supplied by Solvay Advanced Polymers, LLC. Tables 1 and 2 summarize the test conditions for the polysulfone fittings. SEM microscopy, EDX and EDS elemental analysis was performed on the chlorinated water tested specimens following the *Burst* and *Excessive Temperature and Pressure* tests.

Results and Discussion

Chlorine Resistance Testing

The results of chlorine resistance testing are presented in Table 1. The four sets of fittings made from PSU, PPSU/PSU blend, PPSU and glass-reinforced PSU all survived, without failure, to twice the test lifetime of the reference PEX pipe.

Burst Testing

The burst test results are shown in Table 2. All exposed fitting samples tested survived the burst test with the conjoined (new) PEX pipe. The PEX pipe burst, in all cases, above the minimum requirement for burst pressure of the pipe.

Excessive Temperature and Pressure Test

Data of the Excessive Temperature and Pressure Test are presented in Table 3. All exposed fitting and pipe samples tested passed the test.

SEM Analysis

All observations were made on fittings that had been exposed to the chlorinated water followed by the *Excessive Temperature and Pressure* and *Burst* tests. The PPSU material is seen to be the most resistant while the PSU materials the least resistant. The PPSU/PSU blend resistance was seen to be between that of PPSU and PSU materials. This ranking is based on optical analysis using SEM of the exposed, inner layer of the fitting.

Figure 1 shows the PSU fitting in a cross-sectional view toward the inside surface of the exposed fitting. A degraded layer is apparent on the surface. The layer is approximately 20μm thick. Figure 2 shows a magnification of the degraded layer and Figure 3 presents its relative thickness in relation to the entire wall. In this depiction, the degraded layer is shown to be a layer of polymer, 21μm thick, adjoined to the non-degraded, main body of the fitting of 1.5mm thick. This layer of degradation occurred after two test lifetimes of a commercial PEX pipe.

In Figure 4, the degradation layer of the glass re-inforced PSU is presented in a similar cross-sectional view leading to the inside surface. In this case, the degradation layer on the inside surface is seen to be 7μm thick after two PEX test lifetime exposures. Voids are visible through the wall thickness were the glass fibers have pulled out during the SEM sample preparation.

Figure 5 shows a 4μm degradation layer on the PPSU/PSU blend after two test lifetime exposures at the one temperature. The inside surface appears to have localized pitting, approximately 30μm in diameter, with a layered appearance (Figure 6). Based on the observed performance in this paper of the PSU and PPSU materials, it is conjectured that preferential degradation is occurring at the surface of the micro-domains of the PSU within the blend.

The PPSU fitting is shown in Figure 7. It does not show any degradation layer on the inside surface of the fitting. Some micron sized pitting of the surface was observed. Once again, the fitting has undergone two test lifetimes of the PEX pipe at this point.

The degradation was observed for all 4 materials to be a clearly defined distinct layer adjoining the bulk polymer wall. No cracking was observed to extend from this layer into the bulk non-degraded wall.

EDX Analysis

EDX analysis and EDS mapping of the polymer cross-sections showed similar characteristics for all four materials. The oxygen and chlorine concentrations in the degraded surface layer were elevated above the baseline bulk wall levels. Previous research has shown that in non-chlorinated water at elevated temperature, no degradation of the surface occurred[10]. Also no elevation of oxygen and chlorine concentrations was observed in testing with a less aggressive chlorinated water environment at a lower temperature. This is evidence suggesting that the chlorinated water has led to oxidation of the polymer at this temperature**.**

Conclusions

At the test condition, all polysulfone formulations showed excellent oxidative resistance to the chlorinated potable water at the tested condition. The exposure appears to have not affected the mechanical strength of the fittings when compared to the application pipe. Optical analysis has lead to the following ranking, in order of resistance to chlorinated potable water, of the formulations at the test condition:

PPSU > PPSU/PSU Blend > Re-inforced PSU > PSU

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2 K. Oliphant, J. Couch, P. Vibien, A. Chudnovsky, B. Zhang, W. Zhou, *Chlorine Resistance Testing of Cross-linked Polyethylene Piping Materials*, Society of Plastics Engineers Annual Technical Conference (ANTEC), Dallas, USA, 2001.

3 K. Oliphant, J. Couch, P. Vibien, A. Chudnovsky, B. Zhang, W. Zhou, *Assessing Material Performance in Chlorinated Potable Water Applications*, Plastic Pipes XI, Munich, Germany 2001.

4 P. Vibien, S. Chung, J. Couch, J.D. Kim, K. Oliphant, Antec 2003 Environmental Factors In Performance Forecasting Of Plastic Piping Materials, Society of Plastics Engineers Annual Technical Conference (ANTEC), Nashville, USA, 2003.

5 ASTM F876 *Standard Specification for Crosslinked Polyethylene (PEX) Tubing*, ASTM International, USA, 2000.

6 ASTM F2023 *Standard Test Method for Evaluating the Oxidation Resistance of Crosslinked Polyethylene (PEX) Tubing and Systems to Hot Chlorinated Water*, 2000

7 NSF International, *NSF Protocol for Chlorine Resistance of Plastic Piping Materials*, P171, NSF International, USA, September 10, 1999,

8 ASTM D1599 *Standard Test Method for Resistance to Short-Time Hydraulic Failure Pressure of Plastic Pipe, Tubing, and Fittings*, ASTM International, USA, 1999.

9 Gill, L., *Thermoplastic Pressure Piping Compendium,* Canadian Standards Association, Toronto, Canada, 2002.

10 Resistance of Engineering Polymers to Prolonged Hot Water Exposure, BP Amoco Polymers Technical Bulletin G-F-50123 (Mar. 1999)

Table 1: Test Conditions and Results of Chlorine Testing

	Chlorine Test Conditions				Chlorine Test
Material	**Temperature °C (°F)**	**Cl_2 mg/L**	**pH**	**Pressure MPa (psig)**	**Twice PEX Lifetime**
PSU	115 (239)	4.2	6.8	0.4	Non-Failure
PSU/PPSU Blend	115 (239)	4.2	6.8	0.4	Non-Failure
PPSU	115 (239)	4.2	6.8	0.4	Non-Failure
PSU (Glass Re-inforced)	115 (239)	4.2	6.8	0.4	Non-Failure

Table 2: Test Results of Burst Test and Excessive Temperature and Pressure Test

	Burst Test	Excessive Temperature and Pressure Test
Material	**93.3°C (200°F)**	**99°C (210°F), 1 MPa (150psig) Sustained for 48 hrs**
PSU	PASS*	PASS
PSU/PPSU Blend	PASS*	PASS
PPSU	PASS*	PASS
PSU (Glass Re-inforced)	PASS*	PASS
* Attached pipe burst above minimum pipe burst requirement. Fitting did not fail in test.		

Figure 1: SEM of PSU Fitting Cross-Section Showing Chlorine Exposed Inner Surface On The Right Hand

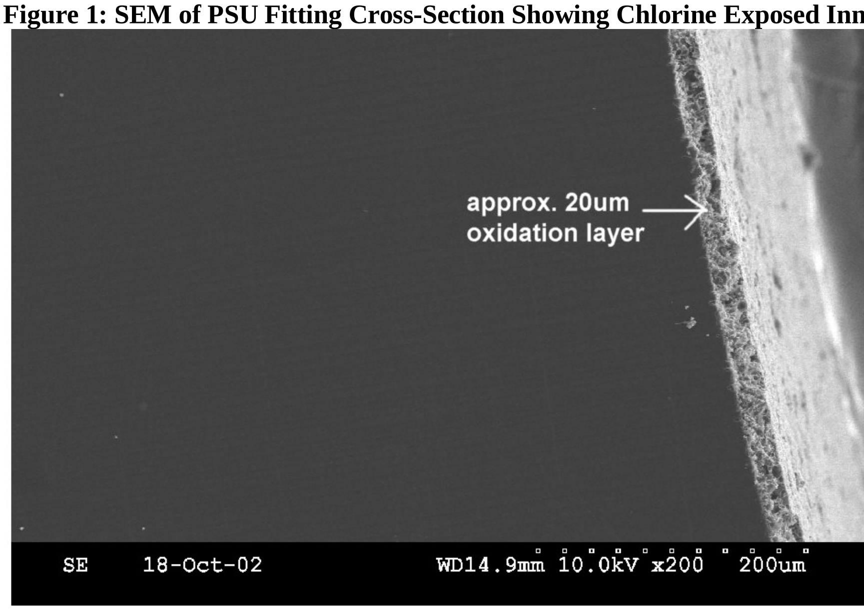

Figure 2: SEM close-up of inner surface oxidation of PSU fitting

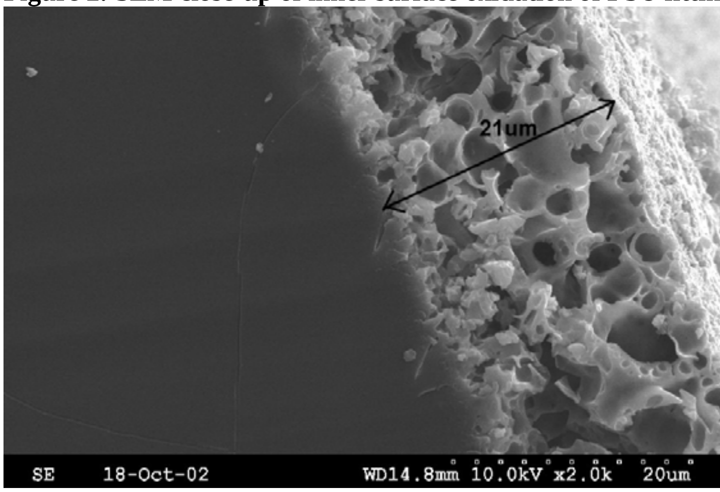

Figure 3: SEM of PSU Fitting Entire Cross-Section Showing Relative Inner Surface Oxidation

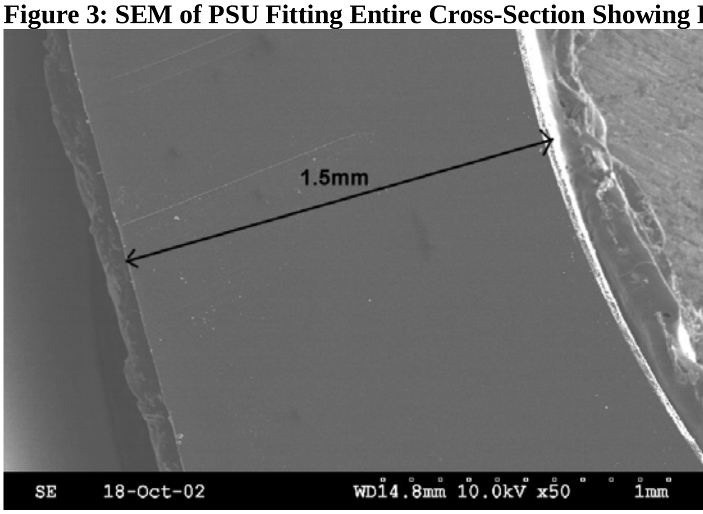

Figure 4: SEM of Cross-Section of Glass Re-Inforced PSU Fitting.

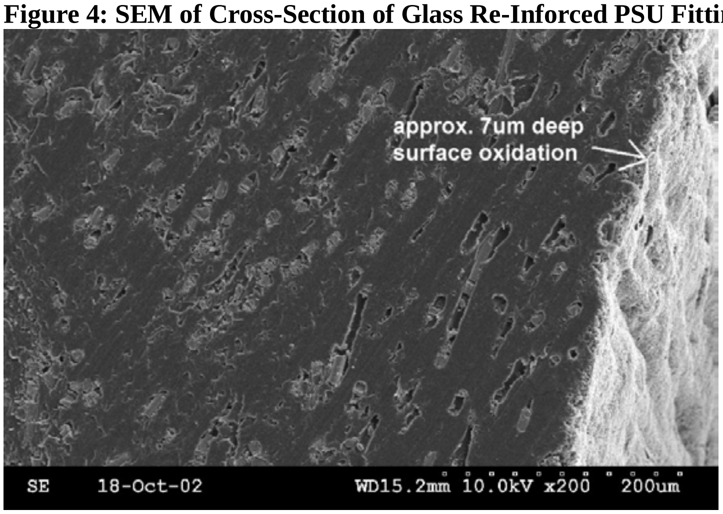

Figure 5: SEM of Cross-Section of PSU/PPSU Blend Fitting.

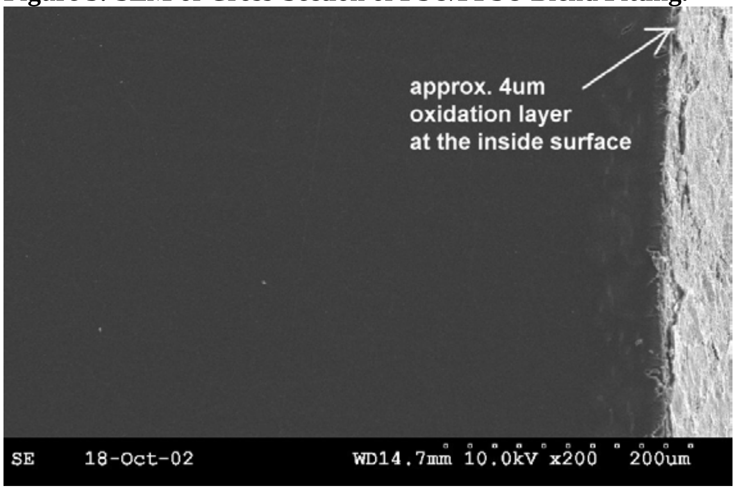

Figure 6: SEM of PSU/PPSU Blend Inner Surface Showing Pitting.

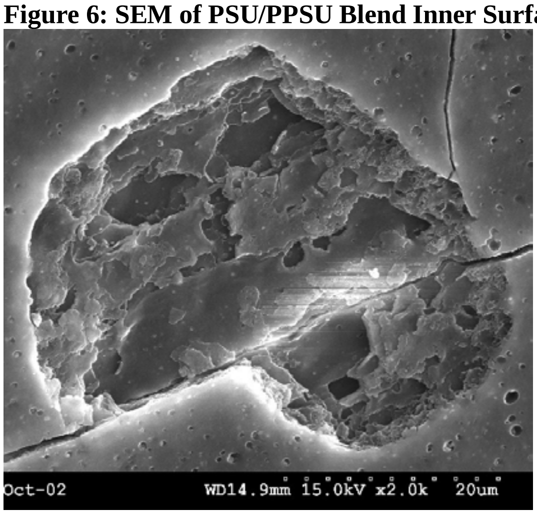

Figure 7: SEM of Cross-Section of the PPSU Fitting.