

Oxidation Resistance of Polypropylene Random Copolymer Pipe to Chlorinated Water

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Abstract Polyolefin pipe is known to be susceptible to oxidative degradation when used in potable water applications. Flowing water inside of such pipe will extract antioxidants from the inside surface of the pipe, causing diffusion-driven migration of more antioxidant from the pipe mid-wall to that surface. Disinfectants in potable water (e.g., hypochlorites, chlorine dioxide, chloramines, etc.) react with antioxidants in the pipe material, decreasing the amount of effective antioxidant until none remains and the polymer is unprotected against oxidation. Also, the response of polyolefin materials to oxidative degradation and the effect of such degradation on pipe performance varies with the different polyolefin polymers. This study presents the results of testing of the resistance of random copolymer polypropylene pipe to chlorinated water and the failure mechanisms observed in the tests.

Keywords Polypropylene · Piping · Oxidation · Regression analysis · Environmental failures · Accelerated testing · Plastics

Background

Polymer piping has become widely used in a variety of applications. Reasons for this widespread use include the fact that plastics are not subjected to galvanic corrosion and therefore do not rust like metallic pipe materials do. Plastic piping materials are resistant to a broad range of different chemical media so that one can find at least one type of

plastic that is resistant to almost any chemical. However, no one plastic material is impervious to attack by all chemicals. Therefore, it is necessary to evaluate the chemical resistance of a specific plastic to chemicals in the end use environment in order to assure that a candidate plastic pipe material will not fail prematurely from chemical attack.

One of the applications where plastic pipe has found significant use is in the transport of water and aqueous solutions including potable water. For potable water, vinyl polymers (PVC and CPVC), polyolefins (polyethylene, crosslinked polyethylene, polypropylene and polybutylene), and assorted other plastics have been employed both as plumbing pipe and buried water distribution pipe (water mains and service lines). These materials must be sufficiently resistant to deterioration by the water itself and by disinfectant chemicals contained in the water to kill water-borne bacteria. For polyolefin piping this requirement translates into a resistance to oxidative degradation of the pipe material by dissolved oxygen in the water and by chemical disinfectants like hypochlorites, chlorine dioxide, and chloramines. These disinfectants, which are added at the water treatment facilities, must persist in the water all the way to the outlets in homes, offices, etc. to guard against contamination from low pressure water leaks and other potential sources of bacteria within the piping and attached appurtenances. Therefore, the polyolefin piping material must be resistant to the disinfectants over the entire length of the piping system, from treatment plant to end user.

The impact that disinfectants have on the extent to which oxidative degradation occurs in polyolefin water pipe and the effects that oxidation has on polyolefin pipe performance varies greatly. All plastic materials are compounded with stabilizer additives to inhibit degradation

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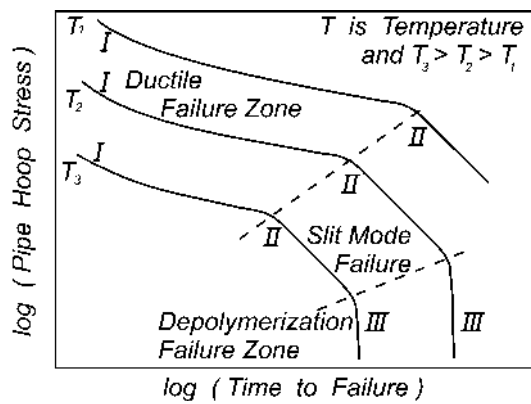


Fig. 1 Three stages of failure in polyolefin pipe creep rupture

reactions that might occur in the material during processing and end use. Antioxidant stabilizers are added to polyolefin compounds for that purpose, and the specific composition of the antioxidant stabilizer “package” in a compound can vary greatly depending upon the end use application. The mechanisms of antioxidant depletion in polyolefin piping have been studied as have the conditions at which stabilizer depletion is significant enough to leave the polymer no longer protected but susceptible to degradation [1, 2]. Oxidation in potable water occurs at the water contact surface, so long as there are disinfectants or dissolved oxygen present in the water.

Once oxidation develops, the impact of degradation on the pipe lifetime can vary dramatically. The effect on polyethylene is surface embrittlement, where once a relatively thin layer of polymer at the affected surface has degraded sufficiently, a crack initiates in the brittle surface layer and propagates relatively rapidly through the pipe wall until leakage occurs [3, 4]. Polybutylene appears to be more resistant to crack propagation and may require continued degradation of the material at the crack tip for a crack to propagate to become a leak. This degradation of the crack tip material to promote crack growth has been observed in the failure of acetal copolymer plumbing fittings. By contrast, acetal homopolymer plumbing fittings have been observed to fail by a dramatic loss of degraded material and a severe reduction in wall thickness. The point here is that different polymers are affected in different ways by surface degradation. Each product manufactured from a different polymer must be evaluated on its own to identify its response to degradation.

It is well understood that oxidative degradation can be the life limiting factor in polyolefin piping performance. This is illustrated in Fig. 1, which is a schematic creep rupture curve for a polyolefin pipe. There are three stages of failure [5]. Stage I occurs at high stresses and short times and the failed specimens exhibit macroscopic ductility. Stage II failure occurs at lower stresses and longer

Table 1 Characteristics of water used in test program

Parameter	Actual value	Control limits
pH	6.8	±0.2
Free chlorine (mg/L)	4.4	±0.2
ORP (mV)	>825	measured
Flow Rate (US gpm)	0.1	±10%

ORP oxidation reduction potential

Table 2 Individual test conditions

Test condition	Specimen #	Temperature (°C)	Pressure (psig)	Hoop stress (psi)	Time to failure (h)
1	1	115	60	145	1679
	2	115	60	143	1715
2	3	115	40	97	1931
	4	115	40	97	1966
3	5	105	80	192	3503
	6	105	80	189	3552
4	7	105	60	144	4034
	8	105	60	144	4096
5	9	95	60	143	8921
	10	95	60	145	7711

times than in Stage I; the leaks in the sample are typically slits or pinholes with no macroscopic ductility. These occur by a different mechanism than Stage I failures. Stage III failures are controlled by degradation (“depolymerization”) of the material. While the magnitude of mechanical stresses can accelerate the rate of oxidation, it can be seen that once the extent of degradation necessary for Stage III failure has been reached, stress magnitude has little effect on failure time. Figure 1 also shows how increasing the temperature affects the stress and time to failure.

Laboratory Testing

A group of commercially available pipe products manufactured from a polypropylene random copolymer material (PP-R) were tested for resistance to an aqueous solution of a chlorine disinfectant widely used in potable water. Samples of pipe that were made in both an unreinforced PP-R and a glass fiber-reinforced (GFR) form were tested. The print line on the unreinforced pipe included the following, “... ASTM F2389 (180F @ 100 PSI) ...” Testing was performed in general accordance with the test conditions of ASTM F2023 [6] and NSF P171 [7]. Water with the characteristics given in Table 1 was continuously circulated through the pipe samples at varying temperatures and internal pressures, which will be identified below. The

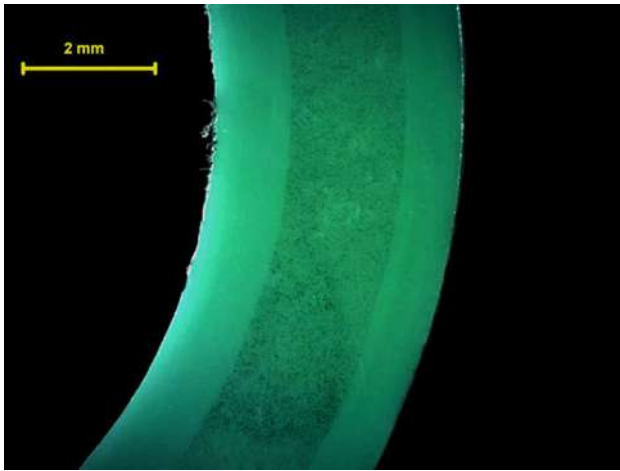


Fig. 2 Cross section of GFR PP-R pipe. Black spots in mid-wall are glass fibers

chlorine/water solution was created by bubbling chlorine gas through reverse osmosis-purified water.

The set of pipe specimens manufactured from an unreinforced PP-R compound was tested at temperatures ranging from 95 to 115 °C and at pressures ranging from 40 to 80 psig. The pipe samples were 20 mm nominal outside diameter with a minimum wall thickness of 3.4 mm (ratio of nominal outside diameter to minimum wall thickness of 6). Duplicate specimens were tested at each of five different temperature/pressure conditions. Test conditions for each individual specimen are presented in Table 2.

Another test was performed on two specimens of a second type of pipe, a multilayer construction reported to have a layer of PP-R on the outside and inside pipe surfaces and a mid-wall layer of GFR PP-R material. Figure 2 shows a cross section of the wall of one of these pipes, viewed with lighting that highlights the glass fibers as black dots in the green-colored PP-R matrix. One can easily see the structure of the pipe wall, with the GFR layer sandwiched between an inner and outer layer of unreinforced PP-R. The water chemistry was the same as in Table 1, but the flow rate was 0.13 gpm. The higher flow rate was necessary because the GFRP pipes were 25 mm nominal diameter (rather than 20 mm) and had a larger inside diameter than the pipes of Table 2. Therefore the test fluid flow rate was scaled according to Sect. 9.1.4 of ASTM F2023. The test temperature was 115 °C, the water pressure was 60 psig, and the hoop stress was 175 psi in one of the specimens and 176 psi in the second. The failure times were 1545 and 1474 h, respectively.

In addition to noting the times to failure of the individual test specimens, the pipes were examined after specimen failure for physical changes. The outer surfaces of the failed specimens were observed to be tacky to the

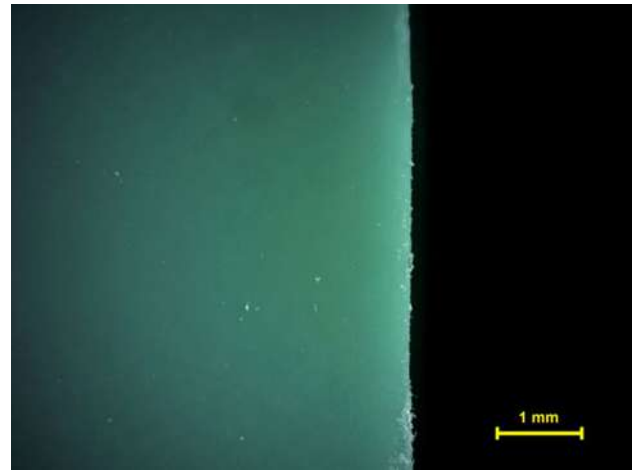


Fig. 3 Interior surface of new, untested pipe

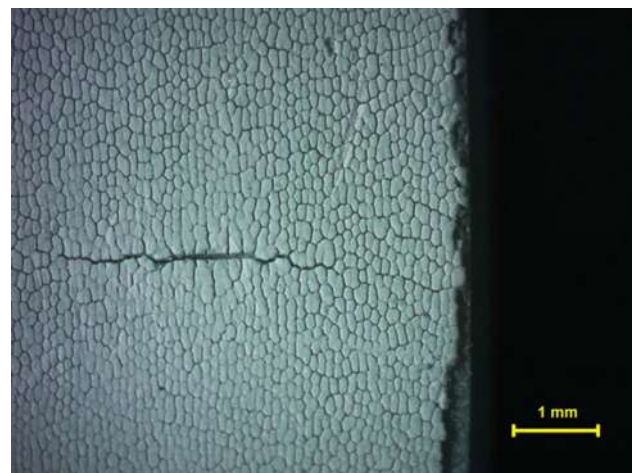


Fig. 4 Interior surface of failed pipe specimen

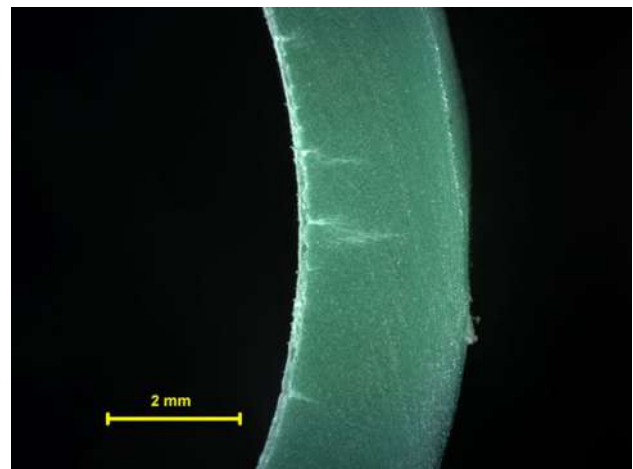


Fig. 5 Radial crack growth from interior wall of failed pipe specimen

touch. The inside surfaces were chalky with extensive micro-cracking and radial crack growth into the pipe walls (Figs. 3, 4, 5). Further, the wall thicknesses of the test pipes

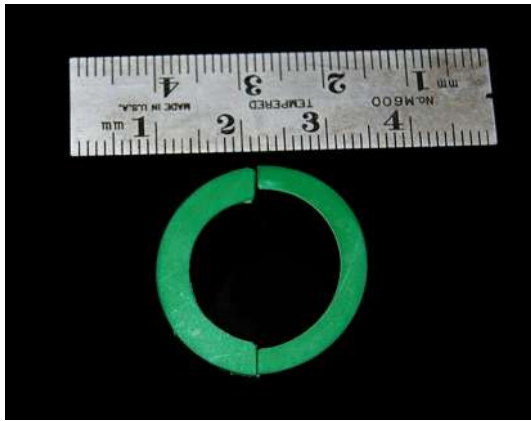


Fig. 6 Wall thickness reduction during testing (untested pipe on left, failed pipe on right)

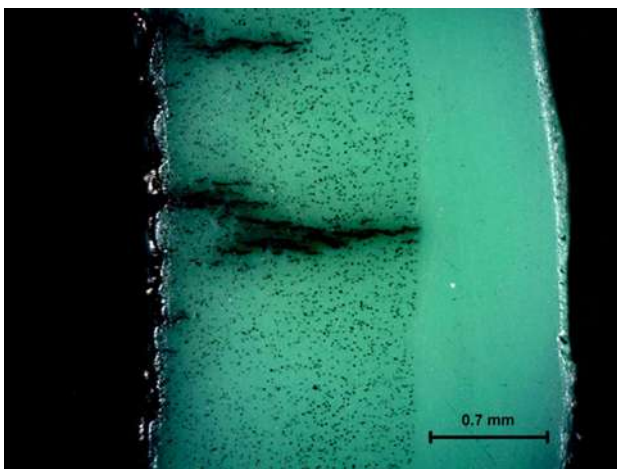


Fig. 7 Cross section of GFR pipe specimen that failed in 1544 h. Black spots are glass fibers

were reduced from their initial values by 35–64%, due to erosion of the flaky inner surface material (Fig. 6). This was also true of the GFR pipes. Figure 7 is a cross section of one of the failed GFR pipes, taken with the same lighting conditions as used in Fig. 2. One can see here that the inner layer of unreinforced PP-R is completely gone, which means that water inside of this pipe would be in direct contact with the GFR layer. Failure of all of the specimens was due to fluid loss through a brittle slit crack in the pipe wall. The presence of cracks propagating radially through the pipe wall can be seen in Figs. 5 and 7.

In order to ascertain whether oxidative degradation of the PP-R material was a factor in the failure of these pipes in the ASTM F2023 tests, infrared spectra of inside pipe surfaces after test failure were obtained by Fourier transform infrared (FTIR) spectroscopy. The instrument was operated in the attenuated total reflectance (ATR) mode, which samples a layer of material only a few microns deep into the surface. Spectra were obtained on the two failed GFR PP-R pipes and,

for control purposes, on one of the GFR pipes before it was exposed to chlorinated water. The spectra are shown in Fig. 8. Figure 9 is an expanded view of the carbonyl region of the unexposed control pipe and one of the failed pipes. It is well known that Stage III failures in polyolefin pipes which occur through oxidative degradation of the polymer create carbonyl groups (carbon–oxygen double bonds) in the polymer that do not exist initially. These carbonyl groups absorb infrared radiation in the range from 1900 to 1550 cm^{-1} [8]. Figure 9 compares the inside surfaces of unexposed and failed pipes. The spectrum of the PP-R material in the failed pipe contains peaks from at least three different carbonyl species, none of which were present in the unexposed pipe material. The most intense of these peaks is at 1713 cm^{-1} and is associated with the formation of ketone species in polypropylene oxidation. The ketone carbonyl peak is usually the most prominent of the carbonyl peaks that appear in oxidized polypropylene.

Discussion

Polypropylene is particularly susceptible to oxidative degradation. Ezrin [9] has noted, “Oxidative degradation occurs readily for both polymers [PE & PP], possibly more so for PP. Contributing to degradation of PP is the fact that every other carbon atom is a tertiary carbon atom ... where both a hydrogen [atom] and a methyl group (CH_3) are located ... Aggravating the degradation of PP is the fact that it degrades primarily by chain scission. PE experiences a combination of crosslinking and chain scission reactions during degradation.” On balance, in PP degradation is more likely to occur than PE because of its much higher tertiary carbon content and the adverse effects manifest sooner with chain scission as the primary degradation result. For these reasons, PP has to be stabilized against oxidation even more so than does PE. Scheirs [10] notes that polypropylene is among the most easily oxidized polymers. Clearly the PP-R pipes tested in this study have been severely oxidized and degraded by the chlorinated water being run through the specimens.

One mechanism that has been proposed to quantify the effect of oxidative degradation on polyolefin pipe performance involves fitting test data like that gathered here to a regression equation of the type shown below in Eq 1 [11]. This equation has come to be known as the “RPM Equation.”

$$\text{Log}(t_f) = A + B/T + (C/T) * \text{log}(S). \quad (\text{Eq } 1)$$

In this equation, t_f is the time to failure in hours, T is the temperature in degrees Kelvin, S is the hoop stress in the pipe, and A , B , and C are the coefficients calculated from a multiple linear regression analysis that fits experimental

Fig. 8 FTIR spectra of inside surfaces of unexposed and two failed pipes

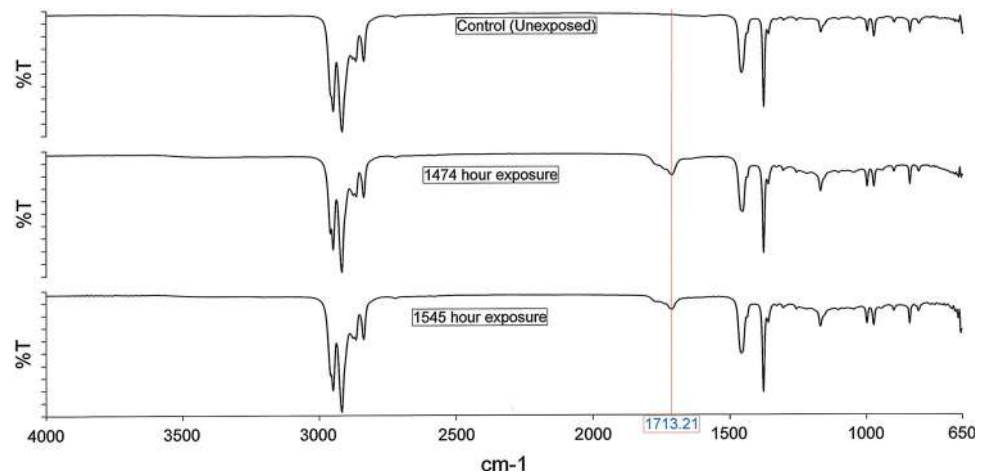
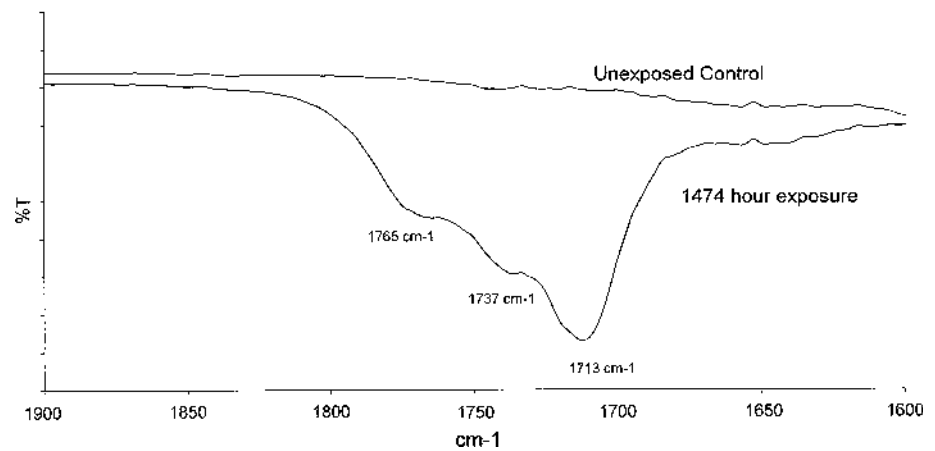


Fig. 9 Carbonyl region of FTIR spectra of unexposed and failed pipes



data to the equation. Such a regression analysis was performed on the data generated from the testing at the Table 2 conditions, using the SigmaPlot 11.0 computer program. A portion of the machine output from this analysis, including an analysis of variance (ANOVA) table, is given in Table 3. The values of the three regression coefficients are $A = -9.425$, $B = 5137$, and $C = -102.4$.

Several statistical tests were performed on the regression analysis results to determine the suitability of the result above for the calculations that are described below [12]. First, the coefficient of multiple determination (R^2) was examined. R^2 indicates how well Eq 1 fits the data within the range of temperatures and stresses employed in the testing. The R^2 value obtained, 0.993, indicates that the RPM Equation fits the test results well. The next test is a test of the regression equation to assess whether or not the coefficients calculated (the numerical values of B and C in Eq 1) actually contribute significantly to the relationship among test temperature, pipe hoop stress, and failure time modeled by Eq 1. This test employs the calculation of a parameter $F_o = (\text{regression mean square})/(\text{residual mean$

square) from the analysis of variance. F_o for this case is shown in the ANOVA section of Table 3. This result is compared to a tabulated value of the F statistic for the desired level of significance of the test. If $F_o > F$ (table) then at least one of the regression coefficients is non-zero and contributes significantly to the model. In this case, $F_o = 466$ while the tabulated value $F_{0.5,2,7} = 4.74$. Thus, at least one of the regression coefficients is non-zero and contributes significantly to the model.

A third statistical test was done to evaluate each of the regression coefficients individually for significance. This test involves calculating a candidate value, t_o , for the values of B and C from the regression analysis. These are shown above in Table 3; $t_o(B) = 23.227$ and $t_o(C) = -2.758$. The hypothesis that the regression coefficient is zero is rejected if the absolute value of t_o for that coefficient is greater than a tabulated value of the t distribution at the desired level of significance and an appropriate number of degrees of freedom. An appropriate value of t from tables of the t distribution is $t_{0.025, 7} = 2.365$. In both cases the absolute value of t_o exceeds the tabulated value which leads to the

Table 3 SigmaPlot 11.0 Output for fit of Table 2 results to RPM Equation

Multiple linear regression	Thursday, November 21, 2013, 2:36:40 PM				
Data source: Data 1 in PP-R nonreinforced					
Log(<i>t</i>) = -9.425 + (5137.142 × 1.0/(col(2))) - (102.452 × col(7)/col(2))					
N = 10					
R = 0.996 Rsqr = 0.993 Adj Rsqr = 0.990					
Standard error of estimate = 0.026					
	Coefficient	Std. Error	<i>t</i>	<i>P</i>	VIF
Constant	-9.425	0.456	-20.653	<0.001	
1.0/(col(2))	5137.142	221.169	23.227	0.001	2.045
col(7)/col(2)	-102.452	37.153	-2.758	0.028	2.045
Analysis of variance					
	DF	SS	MS	<i>F</i>	<i>P</i>
Regression	2	0.608	0.304	465.828	<0.001
Residual	7	0.00457	0.000652		
Total	9	0.612	0.0680		
Column	SSIncr		SSMarg		
1.0/(col(2))	0.603		0.352		
col(7)/col(2)	0.00496		0.00496		

conclusion that both of the regression coefficients (*B* and *C* in Eq 1) are non-zero and contribute significantly to the RPM model of the test data.

The final statistical test is to assess the fit of the data to Eq 1 for making extrapolations beyond the test temperatures and hoop stresses employed in the laboratory testing. This test again employs the *F* statistic [13]. This time *F*_o is defined as the ratio of the “Lack of Fit” mean square to the “Pure Error” mean square from the ANOVA calculations. The model of Eq 1 is concluded to be suitable for extrapolation to temperature and test conditions beyond the bounds of the experimental conditions if *F*_o < *F* (table). The “Lack of Fit” and “Pure Error” mean square values were not part of the SigmaPlot output and were calculated separately. For these data with Eq 1, *F*_o = 2.16 while *F*_{0.05,3,5} = 5.41. This result implies that there is no significant lack of fit of the data to the RPM Equation. The results of these statistical tests all validate the use of Eq 1 with test data of Table 2 to perform the calculations described below.

ASTM F2389 is a standard specification for polypropylene pipe and the pipes tested in this study had that standard number as part of the pipe print line [14]. This standard has a requirement for “Oxidative Stability in

Table 4 Results of lifetime extrapolations from regression equation

Property	Result
Number of data points	10
Coefficient of multiple determination (<i>R</i> ²)	0.993
Pipe size	Nominal diameter = 20 mm, min. wall = 3.4 mm
Extrapolated mean time to failure—continuous use @ 60 °C/80 psig	23 years
95% LCL of continuous use mean	16 years
95% UCL of continuous use mean	31 years
Extrapolated time to failure—intermittent use (25% at 60 °C, 75% at 23 °C)/80 psig	86 years
Extrapolated time to failure—intermittent use (25% at 82.2 °C (180 °F), 75% at 23 °C)/100 psig	10.3 years

Potable Chlorinated Water,” Sect. 8.7. The requirement is that an extrapolation of the test data to 80 psig internal pressure and a constant temperature (e.g. 23 or 60 °C) yield a mean failure time of 50 years. ASTM F2023 also describes performing calculations of extrapolated lifetime for multiple temperature and pressure conditions by use of Miner’s rule [15]. These calculations were performed for the PP-R pipe tested in this program. Details and results of these calculations are given in Table 4.

The calculations summarized in Table 3 show that, for the unreinforced product, the predicted average time to failure at 60 °C (140 °F) and 80 psig internal pressure of 23 years is well below the 50 year requirement of ASTM F2389. Further, the confidence limits of the mean failure time at those conditions indicate that the true mean failure time could be as low as 16 years for continuous use at 60 °C and 80 psig. Because of that segment of the pipe print line noted above—“ASTM F2389 (180F @ 100 psi)” —a lifetime prediction was calculated for intermittent use at that mixture of temperature/pressure conditions. That prediction, of 10.3 years, is also less than the 50 year requirement of ASTM F2389 for intermittent use at 82 °C/100 psig. One further observation is that the average failure time obtained on the two samples of GFRP pipe tested at 115 °C and 60 psig internal pressure (1510 h) is slightly less than the average failure time for unreinforced pipe specimens 1 and 2 in Table 2 above (1697 h), tested at the same temperature and internal pressure.

One final observation about the severe loss of oxidized material from the inside surface of the pipe during use is this. The data analysis described above, utilizing Eq 1, has the hoop stress in the pipe wall as an independent variable. It is assumed in performing a multiple linear regression analysis of test data like that in Table 2 that the stress remains

constant throughout the experiment. However, in the PP-R pipes tested here the wall thickness is changing over the course of the experiment as degraded material is washed away. This results in an increasing hoop stress in the pipe specimens from the beginning of the test until the end. The fact of this progressively increasing hoop stress might possibly invalidate the use of Eq 1 for making predictions of future performance at temperatures and pressures beyond those used in the accelerated laboratory tests.

Conclusions

1. The root cause of the failures PP-R pipe product, both the unreinforced and the GFRP variants, in the ASTM F2023 chlorine resistance testing program was severe oxidative degradation of the PP-R resin compound. This degradation resulted in a substantial loss of degraded material from the interior pipe wall and a consequent substantial reduction of wall thickness of the pipe. A reduced pipe wall thickness would shorten pipe life because of the increase in hoop stress that would result with a fixed internal pressure. Embrittlement of the oxidized PP-R material would also be less resistant to fracture initiation and propagation and would further reduce pipe lifetime.
2. Performance of the multiple regression analysis of ADTM F2023-10, Sect. 13 on the unreinforced 20 mm nominal outside diameter pipe and calculation of a predicted pipe lifetime for continuous use at 60 °C and 80 psig internal pressure yielded the result that this product does not meet the ASTM F2389 requirement for a prediction of 50 years of life under that condition. Further, the lifetime prediction for an intermittent use condition of 82 and 23 °C at 100 psig was only 10.3 years. This last result is far below the 50 year requirement for intermittent use at that temperature/pressure combination.
3. The substantial loss of material from the inside of the pipe specimens during these tests results in an increasing hoop stress in the pipe wall over the duration of the test. This raises a potential question about the use of Eq 1 (the RPM Equation) for the purpose of predicting the life time of PP-R pipe at temperature and pressure conditions beyond those of the ASTM F2023 test. While the statistical tests described above gave the result that the coefficient C did contribute significantly to the model, the absolute value of the calculated t_0 for C (2.758) was only slightly larger than the table value of $t_{0,0.25,7} = 2.365$. If t_0 had been compared to $t_{0,0.1,7} = 2.998$, it would have been concluded that coefficient C was not significant and the regression analysis should have been recalculated without the $\log(s)/T$ term. The rather marginal suitability of the RPM Equation for use with these test data indicates that applying the equation to cases where the hoop stress

in the pipe wall is changing due to significant pipe wall thickness reduction from loss of degraded material might yield unacceptable lifetime predictions.

4. Test results obtained at 115 °C and 60 psig on the unreinforced 20 mm DR 6 pipe and the GFRP 25 mm DR 7.3 pipe yielded essentially the same failure times, in spite of the glass fiber reinforcement layer in the GFRP pipe. It appears that, insofar as chlorine resistance is concerned, the reinforcing layer in the GFRP pipe construction does little to prolong pipe life.

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