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The Effects of Chlorine on Very Low Density Thermoplastic Olefins

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ABSTRACT

In 2007 we became aware of a number of failures of Thermoplastic Olefin Materials (TPOs) that led us to re-evaluate our use of these polymers. We were witnessing the failure of a series of floating covers in both North America and Australia where we had been asked to provide repair and replacement of floating covers and liners. Although the research at that time was concentrating on UV light resistance as a key failure factor; examples of liners failing in the absence of light led us to look at chlorine resistance as an alternative factor.

A key success in our research was the development of a simple test that clearly replicated the failures that we had seen in service. This new test subjected the liner material to a strong chlorine solution at elevated temperature while under stress. This chlorine stress cracking test mirrored the observed steps in the field degradation of TPO materials from loss of stabilizers; to surface cracking; to full failure in a test period of less than 1000 hours. In our evaluation of failed materials we discovered that antioxidant stabilizers were not retaining their effectiveness in the presence of chlorine. Once the stabilizers lost their effectiveness the specimens progressed through predictable degradation stages until cracking occurred.

Once we had developed a background of what was causing the problems in these TPOs we started work on the development of an improved formulation. Through the use of our chlorine stress cracking test we were able to clearly evaluate individual ingredients. This gave us the opportunity to determine which ingredients were causing problems; and, more importantly, gave us a method to optimize the formulation of a replacement material. This paper outlines the development of a chlorine stress cracking test, the results of testing from this test, and the development of an alternative chlorine-resistant TPO formulation as a result of the guidelines provided by this test.

Background

Late in 2006 a customer in Australia lined a potable water tank with a 1.0 mm (40 mil) unsupported flexible Thermoplastic Olefin (TPO) geomembrane. The tank was a 40 m diameter concrete tank (130 ft) with 8 m of water head (26 ft deep). The liner was installed to repair a leaking floor and extended only 1 m (3 ft) up the side walls where it was battened into the concrete side walls of the tank.

The liner was installed in late December 2006 and put into service in January 2007. By June 2007 leakage was observed. Inspection revealed that the liner had cracked through in a number of places and that the peak of all wrinkles in the tank had observable cracks. A large sample (Sample A) was removed for evaluation and testing. The sample revealed that cracks had formed on all small wrinkles that were in the tank. Wrinkles that were only 1 cm (1/2") high were forming cracks.

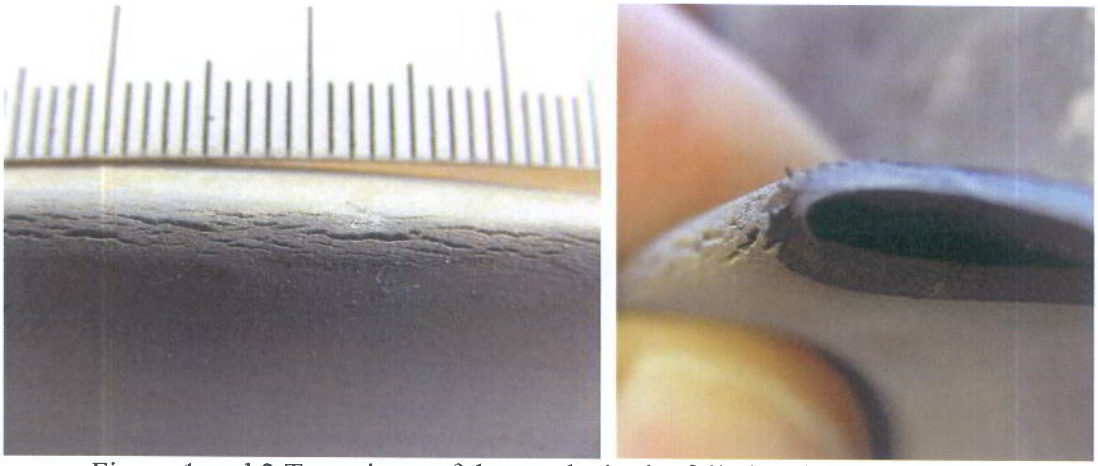

Figure 1 and 2 Two views of the cracks in the failed tank liner material.

Because the liner was in a closed tank without obvious external contamination the first investigation was to see how the liner was damaged. The first testing was to determine the extent and location of the damage. The sample removed from the tank was sent to Canada for testing. All internal areas of the liner that were exposed to the water were damaged while all surfaces on the back of the liner appeared to be undamaged.

Evaluation Testing

The first tests were to determine the extent of the damage in the failed geomembrane. Initial evaluations used the test method Oxidative Induction Time of Polyolefin Geosynthetics by High Pressure Differential Scanning Calorimetry (ASTM D5885 hereinafter referred to as HP OIT). The HP OIT test measures how much heat stabilizer is left in a material. When the value goes to near zero then the material is susceptible to oxidative degradation and failure.

Our lab was unique in that it could use microtome sampling to sample specific surfaces. Using this method we were able to see the differences between different parts of the sample. We were also able to find a retained sample from the actual manufacturing lot (Sample B). Initial testing revealed the following:

Table 1. Initial Evaluation of TPO Sample A

Area Tested	HP OIT Result
Peak of Cracked Area	<5 minutes
Flat Side next to water	16 minutes
Back side away from water	78 minutes
Retained Sample	84 minutes

It appeared that the oxidation stabilizers were being consumed by some agent; however, because of the specifics of this location the only source for the agent was the water. We had extensive water quality data available for this site which showed us that no other chemicals were present except for 1.2 ppm of chlorine. We also knew that UV exposure was not contributing to the damage as this was from a closed dark tank. The liner appeared to be suffering damage from treated drinking water.

Establishing the Failure Hypothesis

At this point we looked into what may have been causing the damage in contact with drinking water. At the same time as we were investigating Sample A from Australia we had been asked to repair two different failures of TPO floating covers in the US. These floating covers were both on potable water reservoirs and had failed substantially after about 6 years of service. Industry associations, such as the Geosynthetic Institute (GSI) were investigating the theory that UV degradation was causing the failures in TPO. In the case of the failed floating covers in the US the UV degradation theory appeared to have merit. In the case of Sample A; however, there was no UV exposure so we felt that some other theory was needed.

At this point we looked into the failures of TPOs in Australia. There had been a number of significant failures and one of the theories was that chlorine contact was leading to oxidative stress cracking. We gathered enough evidence in interviews and discussions with our Australian clients that we felt that chlorine contact may have been a significant problem. We established the hypothesis that the TPO was being attacked by the chlorine in drinking water which was leading to oxidative stress cracking.

Developing an Accelerated Test

In order to determine if chlorine was attacking the TPO we looked at designing a test that would attempt to accelerate chlorine attack and duplicate the failure. After discussion of a couple of possible stress cracking tests our lab suggested that we try the Standard Test Method for Environmental Stress Cracking of Ethylene Plastics (ASTM D1693 Stress Cracking Test). This apparatus is very simple (a test tube with a sample holder) and can be used with any chemicals. The test was run in accordance with the method at a constant temperature of 50C.

The next step was to choose the chemical. There are two methods of adding chlorine to water for disinfection. The first method is to add chlorine gas to the water. The second method is to add sodium hypochlorite (bleach - NaOCl) to the water. In both cases a chemical called underchloric acid (HOCl) is produced which leads to the disinfection of the water. Both chlorine gas and sodium hypochlorite will produce this acid. In our case we chose to use sodium hypochlorite as it is easy to prepare and use in the lab. Selection of the concentration was next. In this case we wanted to challenge the TPO and accelerate testing to the point where we can get a quick result. We chose a 1% (by volume) solution of sodium hypochlorite. This is equivalent to 10,000 ppm. Normal levels of chlorine in water run from 2 to 5 ppm.

There were a number of details that had to be developed to make this test work. First of all the samples needed to be prepared 3 mm (1/8") thick. To accomplish this the lab blended the samples on a two-roll mill and then compression molded them to the thickness needed before cutting to size. The blending, molding, and cutting of all specimens was kept consistent throughout this investigation.

The second issue was how to monitor the residual antioxidant levels in the samples. We selected the HP OIT Test (ASTM D5885) as a way to evaluate the progress of the test. After immersion in the chlorine bath the specimens were removed, washed and allowed to dry for a specific period of time. Then a small shaving of the specimen was removed from the peak of the bent section. This specimen was subjected to the HP OIT test at 170 C under 500 psi of oxygen. A chart is produced that shows heat flow over time. When the heat flow shows a sharp rise the number of minutes to that point is estimated as the oxidative induction time.

Please note that for all future discussions in this paper the samples were immersed in a 1% NaOCl solution according to ASTM D1693 and then removed at selected intervals and evaluated according to ASTM D5885. Unless noted otherwise the test methods followed were the same throughout.

First Round of Testing

The first material that we tested was the TPO retained sample (Sample B). This test was run to see if we could duplicate the failure observed in Sample A. This sample was placed in solution as a bent strip and exposed at 50C. The samples were observed and evaluated at the end of 150 hours, 330 hours, and 840 hours of immersion time. At the end of 150 hours of immersion the HP OIT of the sample fell from 84 minutes to less than 5 minutes. This indicated that the stabilizers were extracted by the NaOCl within the first 150 hours. At the end of 330 hours micro cracks were observed on the surface of the material. At 840 hours of immersion 9 out of 10 specimens had cracked completely. We had duplicated a cracking failure with our accelerated test.

In an effort to confirm if we were observing an oxidative failure we completed infrared spectroscopy scans (FTIR) of the tank damaged material (Sample A) and the material that had been exposed to the NaOCl (Sample B). Both FTIR scans showed evidence of oxidation when compared to the base materials. We ran FTIR tests on the peaks, the exposed surface, and the back side of the tank material. Then we ran FTIR tests on the retained material, the 150 hour immersion, the 330 hour immersion and the 840 hour immersion. It appeared that we had oxidation failures in both the real life samples and the accelerated samples.

At this point we had a theory of the failure and a test that appeared to duplicate the failure in a short period of time. The theory was that chlorine compounds were extracting the stabilizer from TPO geomembrane materials leaving the polymer unprotected from further oxidation or other degradation. We were able to rapidly duplicate this extraction of stabilizers in TPO by using a solution of 1% NaOCl in an ASTM D1693 test and then measuring HP OIT.

Adding Additional Stabilizer

Our next step was to determine whether more stabilizers would provide better protection to the TPO. We added additional stabilizers from our stock additives to the TPO resin to "overload" the polymer with stabilizers. On one of our small film lines our staff made film with no additional stabilizer, then with 2% additional, and then with 3% additional stabilizer. These specimens were sent to the lab where they were subjected to chlorine immersion and HP OIT evaluation. Some of the immersed specimens were also sent to another lab where the actual level of anti-oxidant was determined after chlorine immersion.

The following table shows two types of test results. The first line is the HP OIT results after exposure to NaOCl. The second line is the concentration level of antioxidant as determined by an extraction test.

Table 2. Addition of Extra Stablizer

Antioxidant	As moulded	150 hrs	300 hrs	840 hrs
0% added	55 min 1260 ppm	20 min 1000 ppm		15 min*
2% added	82 min 2020 ppm	20 min 1607 ppm	17 min	20 min*
3% added	81 min 2310 ppm	31 min 2320 ppm	31 min	22 min*

* All specimens showed surface cracking at 840 hours immersion.

There are a couple of things we can see from these results. The first thing we see is that the 0% loading sample retained some HP OIT out to 840 hours. This was an unusual result based on our previous tests. The other thing we see is that adding higher levels of stabilizer did not appear to increase the HP OIT. The 2% and 3% specimens had 82 and 81 minutes of HP OIT respectively. The other thing we see is that the stabilizer levels fell by only 20% in the 0% and 2% specimens but that the HP OIT fell by 60 and 75% respectively. Finally, all specimens at 840 hours showed significant surface cracking. There were no complete failed specimens but all specimens at 840 hours were cracked.

There are a couple of conclusions that we can take from this test. First, the stabilizers are somehow being deactivated, but are not being extracted. The level of stabilizer in the specimens is staying high but the resulting HP OIT is falling very rapidly. Overloading the stabilizer appears to hold the HP OITs a little higher in this exposure test, but the most important result was that at 840 hours surface cracking still occurred. It appeared that antioxidants were not protecting the polymer from cracking at any loading level. Adding additional UV/AO in the form of our standard package was not protecting this TPO material.

A Discussion of HPOIT Applicability

In this last test there appeared to be a higher HP OIT result of 15 minutes out to 840 chlorine immersion hours when previous tests had shown values of less than 5 minutes after 150 chlorine immersion hours. This led us to take look at the HP OIT test. There is quite a bit of debate in the industry of the value of HP OIT testing on TPO materials and there are those, including the resin manufacturer in this case, that felt that the HP OIT test was not a suitable measure of antioxidant levels.

We audited each step in the testing process that our lab was using to conduct these tests and did a series of double checks on various aspects of the testing (comparing HP OIT tests taken within 1 hour of immersion with HP OIT tests taken days later for example). We had also clearly seen in the last test that even though the actual antioxidant was in place the collapse of the HP OIT values showed that cracking of the specimens was imminent. In the end we concluded that the HP OIT was not a perfect measure of antioxidant effectiveness but that it gave us a clear and early indication that antioxidant was about to fail. The first rapid loss of HP OIT values was a clear indicator that antioxidants were about to fail even if subsequent results were less clear.

The key to all of these tests was that we were still seeing actual physical cracking occurring in our stress cracking tests. In the end we felt that HP OIT values of less than 20 minutes were not completely reliable, however a loss of HP OIT from 80 to 20 minutes or less was a clear indication of imminent antioxidant failure.

Addition of Different Stabilizers

The results of our first stabilizer loading test showed us that the current stabilizers we were using were not effective at preventing cracking in TPO even at higher loadings. So for our next set of tests we started looking for suppliers that had specific stabilizer packages that worked differently to protect the polymer. We specifically looked for packages that were developed for TPO resins, for stabilizers with unique chemistry, and for stabilizers that were known to resist extraction. Our additive suppliers also felt that residual catalyst might be causing problems so they suggested that we try a catalyst scavenger to see if it would give us a result.

Table 3. Addition of Different Stabilizers

Antioxidant	No exposure	150 hrs	300 hrs	840 hrs
Control	72 min	15 min	14 min	
Control; Not Bent		28 min	16 min	
Catalyst neutralizer		15 min	12 min	
Phenolic low extraction		16 min	14 min	
Phenolic with DLTDP		13 min	12 min	
Amine-based stabilizer		12 min	14 min	
Phenol and radical scavenger		24 min	15 min	

Unfortunately the attempt to use different antioxidant packages was not successful. As you can see from the table the majority of the additives saw a pronounced drop in HP OIT after 150 and 300 hours of chlorine immersion. There were no significant improvements from these additives.

One additional test that we added during this round of testing was to insert a specimen into the chlorine immersion tubes without bending the specimen in the jig. This un-bent specimen was to see how pronounced an effect that stress was having on the testing. As you can see from the table the effect was minimal.

Finally an additional stress cracking test was run with the TPO specimen in a 5ppm chlorine solution to see if the 1% solution was being too aggressive. The results were HP OIT values of 58 minutes as-received, 20 minutes after 150 hours, and 8 minutes after 300 hours. This was a very interesting result as it showed that the chlorine was clearly the problem at any concentration. Although this result was valuable we stayed with our 1% NaOCl solution for the rest of the testing. This allowed us to compare later results with earlier tests, and we knew that the 1% solution lead to complete cracking failure of materials if the stabilizers were not effective.

Testing New Resins

Having expended considerable effort to find a new stabilization package to no effect we next started looking for alternative resins. We found five potential flexible materials, two were PE-based and two were TPO based. These materials were selected based on their initial flexibility and their ability to be manufactured on our equipment. All materials were blended with a level of antioxidant as recommended by the additive supplier. Flexible TPO Variant 2 did not arrive in time for this initial screening testing. Here are the initial results.

Table 4. New Resin Testing

Material	No exposure	150 hrs	300 hrs	840 hrs
Flexible PE Variant 1	3526 min	911 min	815 min	
Flexible PE Variant 2	3262 min	2153 min	747 min	
Flexible PE Variant 3	3133 min	955 min	634 min	
Flexible TPO Variant 1	36 min	33 min	29 min	15 min
Flexible TPO Variant 2	n/a			

Note that the HP OIT tests on the Flexible PE resins are conducted at a lower temperature (150C instead of the 170C of a TPO test) and give higher minutes of HP OIT than TPO tests. The Flexible PE's did not do particularly well. The Flexible PE variant 1 and 3 lost over 70% of their HP OIT values after 150 hours. Flexible PE variant 2 only lost 30% in the first 150 hours but then was down to 77% lost after 300 hours. This was not the kind of results we were looking for so we set these materials aside.

The surprise here was the Flexible TPO Variant 1. This TPO started off with a low HP OIT value but we had only added 2% of the UV/AO package so that is not unexpected. What's interesting is that this resin only lost 8% of its HP OIT in the first 150 hours, 19% after 300 hours, and 58% after 600 hours. That's pretty much the best performance we had seen to date. What's really remarkable is that the loss of HP OIT is a fairly smooth curve.

Second Test with New Resins

At this point we decided to continue our investigations into the TPO materials. During this period of testing our additive suppliers were also working to try and come up with an antioxidant that would not be deactivated in the flexible TPO resins. After a great deal of investigation and testing on their part they came up with two new antioxidant formulations that they felt would offer significant improvements. These new antioxidants were added to a blend at the additive manufacturer's recommended level and put into the chlorine stress cracking test.

Table 5: New Resin/New Antioxidant Testing

Material	No exposure	150 hrs	300 hrs	840 hrs
Flexible TPO 1 – AO 1	175 min	56 min	49 min	27 min
Flexible TPO 1 – AO 2	79 min	38 min	33 min	
Flexible TPO 2 – AO 1	141 min	74 min	16 min	
Flexible TPO 2 – AO 2	105 min	29 min	18 min	

There are two very interesting results visible in table 5. The first is that the AO 1 is clearly more effective than the AO 2. The other interesting thing is that the as-blended value of the Flexible TPO 1 and AO 1 was for the first time higher than the 80 minutes which has been typical for TPO HP OITs up until this point. This was considered a breakthrough in the development of this product.

In the year following this test result we worked to commercialize the Flexible TPO 1 with the AO 1 additive. Space does not permit complete discussion here of the steps taken to commercialization however the chlorine test was used to evaluate individual ingredients and combinations of ingredients.

Long Term Chlorine Exposure Evaluation

Our final look at chlorine testing was performed once we had our commercial formulation of TPO 1 completed. At this point we repeated our chlorine immersion test with the intent to take the test to a long term result. There were three samples used in this test. The first was the final formulation of TPO 1 with the antioxidant and other additives intended for service in place. The second sample was the original retained sample from the failed batch (Sample B). The third sample was a current commercial product from Competitor 3 molded from a sample of welding rod.

Continuing with the method outlined in our testing above we exposed the samples to a 1% NaOCl solution for 4800 hours. The TPO 1 sample completed this testing without cracking or crazing and with an average retained HP OIT of 49 minutes after 4800 hours of immersion. Sample B lost its initial HP OIT after 150 hours and stress cracked at 900 hours of immersion. The sample from Competitor 3 lost its initial HP OIT values after 150 hours of immersion and cracked after 2400 hours of immersion.

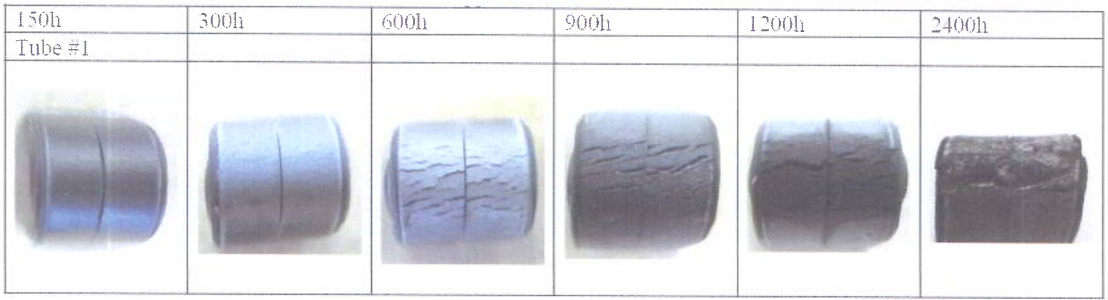

Figure 3: Pictures of Samples from Long Term Immersion Testing on Sample B

150h	300h	600h	900h	1200h	2400h
Tube #1					
					

Figure 4: Pictures of Samples from Long Term Immersion Testing on Competitor 3

150h	300h	600h	900h	1200h	2400h
Tube #1					
					

Figure 5: Pictures of Samples from Long Term Immersion Testing on TPO 1

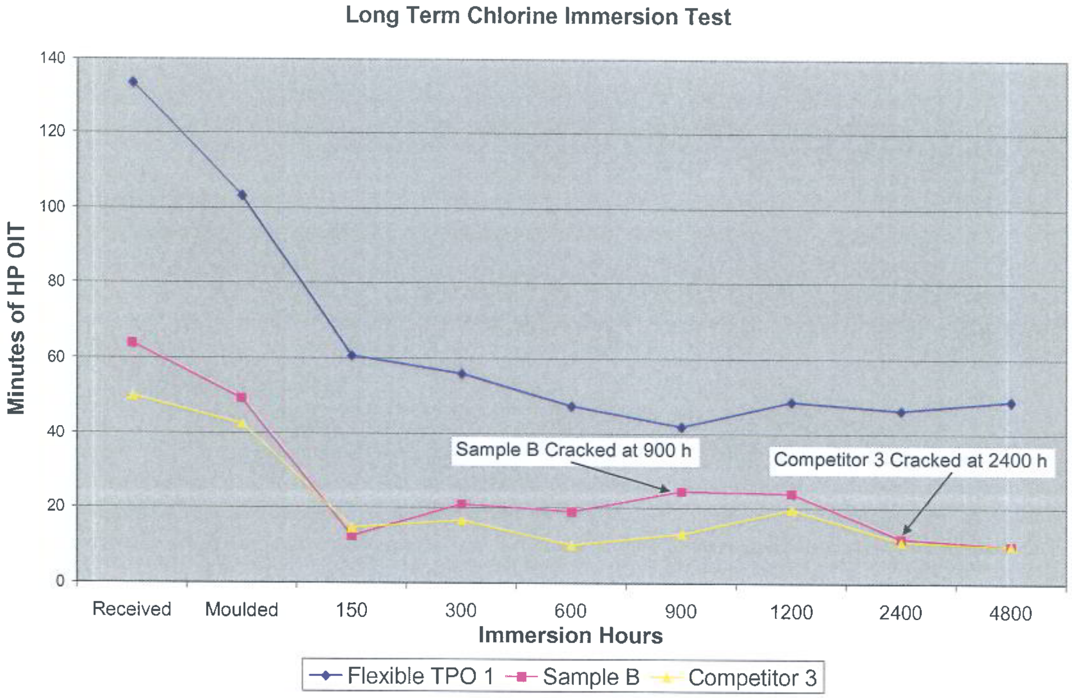

Figure 6; Chart of long term chlorine immersion results.

Conclusions

This paper outlined a new test method that duplicated field failures observed due to oxidative stress cracking in the presence of chlorine. We demonstrated that the original TPO material was difficult to stabilize either with additional stabilizers or different stabilizers. Extraction tests showed that the stabilizers appear to remain in the polymer however they are being deactivated by chlorine contact leading to oxidation and stress cracking failures. The combination of the stress cracking test using 1% NaOCl and an HP OIT evaluation gave us a potent tool for evaluation of new resins and additives when designing for potable water containments.

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